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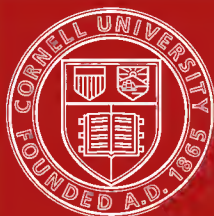
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DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH

*Dept. of Dairy Industry
N. Y. S. Col. of Agr. at
Cornell University.*

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The Physics and Chemistry of
COLLOIDS
and their bearing on Industrial Questions

Report of a General Discussion
held jointly by
THE FARADAY SOCIETY
and
THE PHYSICAL SOCIETY OF LONDON

ON 25TH OCTOBER 1920



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PREFATORY NOTE

In view of the growing industrial importance of Colloidal Physics and Chemistry and with the intention of surveying critically the present state of knowledge as an aid to future development, the Councils of the Faraday Society and the Physical Society arranged a joint Conference on the subject which was held on the 25th October 1920.

It was realised that the Conference would fail of its desired effect if a full report of the proceedings were not published, but the two Societies concerned were unable to incur the expenditure which publication would involve. Application was accordingly made to this Department for assistance, and it was decided on the recommendation of the Advisory Council that in view of the exceptional scientific and industrial importance of the matters dealt with in the report, it should be published for the Department by H.M. Stationery Office.

It must be understood that in these circumstances the Department of Scientific and Industrial Research accepts no responsibility for the statements of opinion or fact contained in the report.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH,
16 and 18, Old Queen Street,
Westminster, London, S.W.1.

October, 1921.

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THE FARADAY SOCIETY
AND
THE PHYSICAL SOCIETY OF LONDON.

THE PHYSICS AND CHEMISTRY OF COLLOIDS AND THEIR
BEARING ON INDUSTRIAL QUESTIONS

A GENERAL DISCUSSION

At a joint meeting of the Faraday Society and the Physical Society of London, held on Monday, October 25th, 1920, in the Hall of the Institution of Mechanical Engineers, London, a General Discussion took place on "The Physics and Chemistry of Colloids and their Bearing on Industrial Questions."

Sir Robert Hadfield, Bart., F.R.S., President of the Faraday Society, opened the proceedings at 2.30 p.m., after which the chair was taken by **Sir William Bragg, K.B.E., F.R.S.**, President of the Physical Society of London.

A General Introduction to the Discussion, entitled "A Short Survey of the Physics and Chemistry of Colloids," was delivered by **Dr. The Svedberg**, Professor of Physical Chemistry in the University of Upsala.

A SHORT SURVEY OF THE PHYSICS AND CHEMISTRY OF COLLOIDS

BY

DR. THE SVEDBERG,

PROFESSOR OF PHYSICAL CHEMISTRY, UNIVERSITY OF UPSALA

The science of colloids is a science of the microstructure of matter. In it is reflected the tendency of modern natural science to deal more and more intensely with the problem of structure in its full extent. In the great science of the structure of matter, the science of colloids forms the domain that lies above molecular dimensions and beneath macroscopic dimensions. In this domain we have a great number of those systems which are the basis of our material culture and the basis of life as a whole. All living beings are built up of colloids; almost all our food, our articles of clothing, our building materials, are colloids. Or, to mention some special systems, protoplasm, proteins, glue, starch, all kinds of fibres, wood, brick, mortar, cement, certain kinds of glass, rubber, celluloid, &c. The importance of colloid science for many industrial questions is, therefore, beyond all doubt.

The science of colloids is a rather young one. The field of study which it concerns has for a long time been disregarded. In order to be able to treat with success all the questions presented to us by industry, there is still much to be carried out in the department of pure colloid science. In what follows, I will try to give a short review of the scientific results so far obtained and of the problems which, in my opinion, need especial attention.

The various branches of colloid science are connected to such an extent that it is very difficult to treat the different questions separately. We will try to fix our attention on two principal problems: (1) the *formation of colloids*, and (2) the *changes of structure* in colloid systems. Connected with both these is the problem of the *properties of colloids* and the changes in these properties during the processes mentioned under (2).

The formation of a colloid may be effected in two ways, different in principle, viz., by *condensation* and by *dispersion*, according as one tries to obtain a microstructural system, a colloid, from a molecular structural or a macrostructural system.¹

In the case of a condensation process, the degree of "graininess" or the degree of dispersion² will become higher as the degree of supersaturation increases; which must, of course, always precede condensation. This is the case when fogs are formed by adiabatic expansion of gases,³ e.g. cloud-formation in the atmosphere, when metal colloids are prepared by condensation of metal gas from the electric arc,⁴ when a slightly soluble substance, e.g. barium sulphate, is precipitated by means of a reaction between ions.⁵ The condensation always proceeds from certain heterogenities in the medium; condensation centres or nuclei. As such nuclei, we may have particles of the substance which is to be formed by the condensation, e.g. precipitation of gold on small gold particles⁶ when preparing gold hydrosols or gold ruby glass, or gas ions,⁷ e.g. fog-formation in gases

at low degrees of supersaturation, or complex molecules, *e.g.* fog-formation in gases at high degrees of supersaturation. The manner in which these nuclei are introduced into the system under condensation is of great importance for the degree of dispersion of the colloid resultant.⁹ If the nuclei are not introduced into the system all at once, but gradually in the course of the condensation process, the particles will be very unequal in size.

The biologically important colloids, *e.g.*, the proteins, are evidently all formed by condensation, but no details of this process are known. The tendency towards condensation manifests itself in the fact that even the protein molecules are, from a purely chemical point of view, condensation products.⁹

In case of a dispersion process, there is always work to be performed against the surface tension or the cohesion force. Accordingly, such a process is, in contradistinction to a condensation process, a forced and not a spontaneous one. We know very little as to the relation between degree of dispersion and experimental conditions. When emulsifying fats and hydrocarbons, the surface tension may be lowered by the addition of small quantities of alkalies or soaps.¹⁰ Grinding, in general, does not lead to a very high degree of subdivision; but it is possible to increase the latter by adding an indifferent solid diluent which can easily be dissolved and removed, leaving the disperse phase suspended in the solvent used.¹¹ Thus, colloid sulphur has been prepared by grinding sulphur with urea and putting the substance in water.¹² A combination of grinding and chemical effects on the material may also be used.¹³ It seems that, in many cases, a prevention of the aggregation of the particles by means of suitable additions ought to render possible the preparation of high disperse systems by pure grinding.

Bubbles and foam might be regarded as a kind of colloids formed by dispersion. On spontaneously breaking up, they form new disperse systems in which the phase that was previously the continuous one becomes the non-continuous one, and *vice versa*. The system: "soap foam — air," with the soap solution as the continuous and the air as the non-continuous phase, is transformed, on account of surface reduction *i.e.* condensation, into the system: "soap solution drops — air," with the air as the continuous phase. Mercury foam in water (produced by means of pressing water through mercury) breaks up into a mercury hydrosol partly very fine-grained.¹⁴

A newly-formed colloid may, immediately after its formation, undergo changes of structure of a more or less profound nature. On the other hand, it is nearly always possible to prevent the occurrence of such changes, and therefore we have a right to distinguish and investigate the *primary structure* as the direct result of the colloid-forming process.¹⁵ Colloids with primary structure may conveniently be called *primary colloids*.

We have at our disposal several methods for the closer study of the structure. Almost every property of a colloid depends on the structure, and therefore, conversely, from the study of the properties of colloids we may draw conclusions as to their structure.

The most important and most obvious means is the microscope and the ultramicroscope.¹⁶ With their aid, it is often possible to settle whether the colloid under investigation is of a grainy structure, *e.g.* a colloid gold solution in water, a gold hydrosol, or of a foamy structure, *e.g.* high disperse soap foam, or of a fibrous structure, *e.g.* soap solutions of certain concentrations. The number and

approximate size of the discontinuities, *e.g.* the particles, may also be determined in this way. One may, for instance, count in the ultramicroscope the number of particles observed in a certain volume of gold hydrosol, and by means of analysis determine the content of gold present in the sol. From these figures we get the mass and approximate size if, for instance, we make the assumption that they are spherical. On the other hand, the ultramicroscope gives little or no information about the form or structure of the particles.¹⁷

A means of deciding whether the particles are symmetrical is to be found in the study of the behaviour of the colloids in magnetic or electric fields.¹⁸ Non-symmetrical particles are oriented by such fields and thereby impart to the colloid a certain, though in general very slight, degree of double refraction, which may easily be measured with great accuracy. In this way, we have been able to settle that the particles in common sulphur hydrosols, prepared by oxidation of hydrogen sulphide, are spherical; but sulphur hydrosols, prepared by grinding sulphur with urea, are unsymmetrical. The particles in gold hydrosols prepared by reduction are unsymmetrical to a high degree.¹⁹

Two other optical properties, *viz.*, the light absorption and its accompanying phenomena, the scattering and polarisation of light—the Tyndall phenomenon—may also in certain cases be used for structure studies.²⁰ Theory, as well as practice, proves that these phenomena are, for instance, dependent to a great extent on the degree of dispersion of the sol. The form and structure of the particles also influence the said properties, but in a manner hitherto unknown. The emission of light from illuminated particles especially—the Tyndall light cone—varies to a great extent with the size of the particles or the degree of dispersion.²¹ Colloid solutions that contain very small particles, *e.g.* Faraday's gold hydrosols, give only a slight emission; the light cone is scarcely visible. Those with large particles, *e.g.* gold sols made from Faraday's gold sols by allowing the particles to grow in a reduction mixture, emit very much light; the Tyndall cone is very prominent. The optical properties of the particles also play a great part. Thus metal particles emit much light, particles of silicic acid or of gelatin only a little.

The resistance exerted on the particles by the surrounding medium when they move under the influence of a force is a means of investigation that is now often used for the determination of the size of the particles. In some cases, *e.g.* when a sol is filtered through a membrane of collodium or gelatine (ultrafiltration²²), the connection between the resistance and the size of the particles is not known in detail, but we are justified in assuming that the resistance rises with the size of particles. The small particles are more rapidly pressed through the filter than the large ones.²³ Certain kinds of filters transmit molecularly dissolved substances, but not colloids; an important method of separation, especially in biochemistry. If a colloid is separated from a great quantity of dispersion medium by such a membrane, the molecularly dissolved substances—the crystalloids—diffuse through the membrane, leaving a colloid of a purer state—Graham's dialysis.²⁴ If the particles are spherical and move through a liquid, the resistance is $6\pi\eta rv$, where η is the viscosity, r the radius and v the velocity. If the force that causes the movement is known, *e.g.* gravity, the radius may be calculated.

Thus, by measuring the velocity of sedimentation, the radius can be found.²⁵

We have

$$r = \sqrt{\frac{9\eta v}{2(s_1 - s_2)g}}$$

where s_1 is the specific gravity of the particle, s_2 that of the liquid, and g the gravity constant.

Even when no exterior forces are acting, the particles in a colloid solution are in movement because of the impacts from the surrounding molecules. This is the so-called Brownian movement, which has attracted so much attention of late.* According to the kinetic theory of the Brownian movement, which has been fully confirmed experimentally, each particle, whatever its size and nature, has the same translatory energy as a molecule, i.e. $\frac{3RT}{2N}$, where R is the gas constant,

T the absolute temperature, and N the Avogadro constant. Because of the resistance of the surrounding medium, the mean value of the square of the distance traversed in the time t by the particle is $2Dt$, where D , the diffusion constant of the particles, has the value $\frac{RT}{N} \cdot \frac{1}{6\pi\eta r}$. Thus, if the displacement of the particle is measured the radius may be found. In certain cases it is more convenient to measure D directly and then calculate r by means of this experimental value.

Owing to the fact that the size of the particles is rather great in comparison with that of the molecules, colloids diffuse very slowly compared with crystalloids. As a matter of fact, Graham, the founder of colloid chemistry, regarded this property as the fundamental difference between colloids and crystalloids. We know now that between colloids and crystalloids—so very different in their extremes—there exist all degrees of transition forms, and therefore all degrees of diffusibility.

The size of particles may also be determined by measuring the sedimentation equilibrium, i.e., the distribution of the number of particles per c.c. under the joint influence of gravity and the Brownian movement. In this equilibrium, the concentration of the colloid diminishes exponentially with increasing height, as is the case with the atmosphere surrounding the earth.

We have

$$n_2 = n_1 \cdot e^{-\frac{N}{RT} \cdot \frac{4}{3} \pi r^3 (s_1 - s_2) g (x_2 - x_1)}$$

where n_1 is the number of particles at the height x_1 , n_2 that at the height x_2 .

Hence

$$r = \sqrt[3]{\frac{RT}{N} \cdot \frac{\ln \frac{n_1}{n_2}}{\frac{4}{3} \pi (s_1 - s_2) g (x_2 - x_1)}}$$

The osmotic pressure of a colloid solution is determined, as far as the colloid in it is concerned, only by the number of particles per c.c. (n).

We have

$$p = \frac{RT}{N} \cdot n.$$

Consequently, the osmotic pressure is a measure of the degree of dispersion. The osmotic pressure of a colloid is often determined by means of a common osmometer, provided with a membrane permeable to crystalloids, but impermeable to the colloid particles.²⁷ Now, however, owing to ion adsorption, the particles are, in most cases, surrounded by an electric double-layer of ions, and the colloid thus acts as an electrolyte, one ion of which is able to penetrate the membrane, but not the other. This causes complications. A so-called membrane equilibrium is formed, and the osmotic pressure found is not a real measure of the structure of the colloid.²⁸

Owing to the Brownian movement, the number of particles in every small volume of a sol undergoes spontaneous and incessant fluctuations. Hence the value of every property of the colloid in the small volume fluctuates.²⁹

We have

$$n = \frac{e^{-\nu} \nu^n}{|n|}$$

where n is the momentary value of the number of particles in the small volume ν and ν the mean value.

This phenomenon, predicted by the kinetic theory for colloidal as well as for molecular solutions, has been the subject of extensive investigations. The results are of importance because they show that Boyle's law holds good very exactly for dilute colloid solutions, and because of the light they have thrown on the applicability of the probability calculus to a natural phenomenon. From these studies we have also obtained a deeper comprehension of the conception of entropy. For they have shown, in a direct and experimental way, that the law of the incessant growth of entropy only holds for macroscopic systems.³⁰

It often occurs that the particles of a colloid are too small to be measured directly, *e.g.* by means of the ultramicroscope or by determining the velocity of sedimentation. In some of these cases one can overcome the difficulty by depositing gold on the particles, thus increasing their size.³¹ This method has already been applied to sols of almost all the metals and to sols of some sulphides.³² If the quantity of gold on a particle is known, it is easy to calculate the radius in the usual manner.

In most colloid solutions and precipitates there are particles of various sizes, and the investigator should, of course, be able to determine not only the mean size, but also the real structure of the sol, *i.e.* the law governing the distribution of the various sizes of particles.³³ Among the phenomena reviewed above only the velocity of sedimentation, the sedimentation equilibrium, and the Brownian movement have been used in studying the distribution of the size of the particles. On the basis of the former phenomenon just mentioned a method has been worked out which has already provided us with much valuable information as to the formation of the various particles in colloids and the agglomeration processes taking place in them.³⁴

Finally we will consider two phenomena, the study of which does not, it is true, enable us to carry out direct measurements of the structure, but which, in spite of that, are of great interest in judging of the structure of colloids, *viz.*, the viscosity³⁵ on the one hand, and, on the other, the adsorption³⁶ and the accompanying phenomena, *viz.*, the cataphoresis³⁷ and the electric endosmose.³⁸

The viscosity of a sol depends, in a manner not yet known, on the size of the particles, the concentration, &c., but above all on the nature of the particles. Some sols, *e.g.* metal hydrosols, suspensions of barium sulphate (Case 1) have a viscosity only slightly greater than that of water, but others, *e.g.* silicic acid hydrosol, oil emulsion, gelatin solution (Case 2) have a viscosity many times greater than that of water. From the fact that suspensions with undoubtedly solid particles come under Case 1 and emulsions with undoubtedly fluid particles come under Case 2, the conclusion has been drawn that the fine-grained colloids under Case 1 also contain solid particles and those under Case 2 fluid ones. If this be the case, measurements of the viscosity would be a capital means of ascertaining the state of aggregation of the substance of the particles. Recent investigations indicate, however, that the case is far more complicated. Small particles probably have relatively thicker water-coverings than greater particles, and, accordingly, the viscosity is higher in a fine-grained colloid than in a coarser one, provided the two sols have particles of the same material and are of the same concentration by weight (*e.g.*, sulphur hydrosols). When the potential difference between particles and fluid is altered the thickness of the water-coverings should alter and, as a matter of fact, the viscosity is altered too. As the water-covering increases, the particle will act more and more like a drop of fluid in relation to the surrounding medium and will, therefore, as far as the viscosity is concerned, approach more and more to the limiting case which is represented by an oil emulsion.³⁹

The phases—two or more in number—in a disperse system have a contact surface very large relatively to the volume of the system. It is obvious that in such circumstances adsorption plays a prominent rôle. The adsorption of different substances differs in strength. If an electrolytically-dissociated salt is adsorbed, cations and anions are, of course, brought together at the contact surface in equal numbers, but the adsorption of the particles in relation to cations and anions is most often unequal, inasmuch as one is present in excess nearest to the surface of contact and the other in excess some way out in the liquid⁴⁰. The result is the formation of an electrical potential difference, a so-called adsorption potential difference or an electrical double-layer. Because of this the disperse phase, when exposed to the influence of an electric field, will migrate towards one of the poles, provided it is freely movable, as in the case of a colloid solution (cataphoresis). If the disperse phase is immovable the liquid will move in the opposite direction (electrical endosmose). By measuring the velocity of migration of the particles or the liquid under various conditions we are able to study the changes in the difference of potential and thereby in the adsorption. At least at low concentrations the adsorption may be expressed by the formula

$$y = a \cdot c^{\beta}$$

where y is the amount of substance adsorbed per gr. adsorbent, c the concentration in the solution of the substance adsorbed, and a and β constants depending on the nature of both. Now, as a rule, it happens that for the two ions of a salt both a and β have different values, *e.g.*

$$\begin{aligned} a_{\text{cation}} &< a_{\text{anion}} \\ \beta_{\text{cation}} &> \beta_{\text{anion}} \end{aligned}$$

In the example chosen the disperse phase will with increasing adsorption become more and more negative in relation to the dispersion

medium. This charge reaches a maximum and decreases to zero, at the point where the adsorption isotherms intersect, then becomes positive and increases again⁴¹.

The changes of state which may occur in a disperse system, a colloid, are essentially changes of structure⁴². Of course, purely chemical reactions, too, are to be taken into consideration, but they do not play such a prominent part here as in the molecular structural systems. The greater number of the disperse systems, and those of greatest importance too, are the ones whose disperse phase is embedded in the other phase in the form of particles; in the sequel we will only mention the changes of state in such systems. The most important change of state is the uniting together of the single particles (primary particles) into aggregates (secondary particles). Such an aggregation often occurs directly after the formation of the particles. It may stop for various reasons after the aggregates have reached a certain size. The result is a colloid with complex particles—a *secondary colloid*. If the aggregation goes on further we may have two extreme possibilities—with many transition forms.

FIRST CASE: one or more of the following factors dominate, viz. :—

- (1) Low hydration of the particles.
- (2) Low number of particles per unit volume.
- (3) Great difference in specific gravity between particles and liquid.
- (4) Violent stirring of the system.

The characteristic of this case is that no bridges are formed between the aggregates and that, in consequence of this, they fall to the bottom after having grown sufficiently; *the colloid is precipitated* (e.g. coagulation of a gold hydrosol by the addition of hydrochloric acid).

SECOND CASE: one or more of the following factors dominate, viz. :—

- (1) High hydration of the particles.
- (2) High number of particles per unit volume.
- (3) Small difference in specific gravity between particles and liquid.
- (4) No stirring of the system.

In this case bridges are formed between the aggregates, and the particles arrange themselves into a three-dimensional network throughout the system: *the colloid gelatinizes* (e.g. the coagulation of a sol of silicic acid by the addition of hydrochloric acid, the setting of a warm gelatine solution when cooling). Owing to capillary forces the liquid is kept in the network with great strength. Measurements have shown that the liquid is under a pressure of several hundred atmospheres. In many respects, therefore, the gelatinized colloid acts as a solid.

There exist numerous transition forms between these two extreme cases. If the particles are not bound together by bridges into a solid, but still reach macroscopical size and possess a certain loose structure, one speaks of *flocculation of the colloid* (e.g. coagulation of ferric hydroxide hydrosol by addition of ammonia). It may be doubted, however, if such flocculent suspensions are not to be regarded as fragments of a gel of little mechanical resistance shattered by the stirring of the liquid. Several observations support the view that there is in all colloids a certain tendency towards the formation of

a network structure, the network being, however, in such systems as approach CASE 1, very easily destroyed by movements in the liquid. In CASE 1 the Brownian movements alone of the particles should suffice.

The most important cause of the aggregation of the particles is the decrease or the disappearance of the difference of potential between particle and liquid. This may be effected by altering the ion adsorption. Hence one of the most important means of bringing about aggregation or disaggregation is: *addition or removal of ions*. Because of the opposite electric and coagulating action of anion and cation and their difference of adsorption there will always exist, for certain electrolytes in relation to a certain colloid, a domain of concentration within which they have a disaggregating action. If a solely aggregating electrolyte is added to a colloid in increasing doses (*e.g.* hydrochloric acid to a gold hydrosol), the velocity of aggregation first rises rapidly with concentration, then more slowly and reaches a constant maximum value⁴³. Let us make the assumption that within the latter region *every* mutual approach of two particles to a certain limit leads to aggregation, but within the former region only a certain *fraction* of those approaches. Then it is possible to develop, on the basis of the laws of the Brownian movements alone, a mathematical theory for the kinetics of aggregation. The formulæ for the decrease in the number of single particles (primary particles), and for that in the total number of particles (primary particles + aggregates) have been verified experimentally.⁴⁴

We have—

$$\nu_1 + \nu_2 + \nu_3 + \dots = \frac{\nu_0}{1 + \beta t}$$

$$\nu_1 = \frac{\nu_0}{(1 + \beta t)^2}$$

where—

ν_0 = original number of particles.

ν_1 = number of single particles after the time t .

ν_2 = number of double particles after the time t .

ν_3 = number of triple particles after the time t .

$\beta = 4\pi DR\nu_0$.

D = the diffusion constant.

R = the distance to which the particles must approach if there is to be any aggregation.

With regard to the aggregation by electrolytes it has, in addition, been found that inorganic ions of the same valency generally aggregate equally strongly if added in equivalent amounts⁴⁵. This is due to some extent to their being nearly equally strongly adsorbed. When the valency of the aggregating ion increases the aggregating effect rises very rapidly⁴⁶. The concentrations of the ions $K \cdot Ba \cdot Al \dots$ required to aggregate particles of As_2S_3 to the same degree show the mutual relations: 1, 1/20, 1/1000. Thus the three-valent $Al \dots$ has an aggregating power 1,000 times greater than the mono-valent K . These circumstances are closely related to the course of the adsorption isotherm, but are not yet quite clear⁴⁷.

The aggregation may be reversible or irreversible, *i.e.*, in certain cases disaggregation may be effected, in others not. Some colloids (*e.g.*, metal hydrosols) are difficult to disaggregate, others (*e.g.* sulphur hydrosols) are easy. Certain ions nearly always bring about

irreversible, others reversible aggregation. The question of irreversible or reversible coagulation is probably closely connected with that of the hydration of the particles. Thus particles which hold much water around them are easily disaggregated. The water-covering prevents the particles from uniting too closely together.

The aggregating effect of an electrolyte may often be reduced to a very great extent by the addition of a small quantity of a suitable colloid of another kind only slightly sensitive to electrolytes, a so-called protective colloid, *e.g.* gelatine to a gold hydrosol.⁴⁸ As a rule the electric charge of the protective colloid should be of the same sign as that of the colloid to be protected. The mechanism of this protecting action is still but very incompletely known. Most probably the particles of the protective colloid become attached to the particles of the other colloid and the aggregate resulting from this obtains a good deal of the stability towards electrolytes which characterises the protective colloid. Colloids of opposite electric charge precipitate each other mutually (*e.g.* the negative Sb_2S_3 and the positive Fe_2O_3) provided there is not too great an excess of either of them, in which case no precipitation will occur⁴⁹. This is obviously entirely analogous to the action of the ions. Such mutual colloidal reactions are of great importance in the economy of nature and in industry.

In the preparation of easily aggregated colloids a protective colloid is often added in order to maintain the primary structure. Thus the particles of a metal hydrosol, if formed in the presence of a small quantity of a protective colloid, are kept apart even when the sol is evaporated to dryness. The dry substance can be redissolved in water without any perceptible change of structure taking place (*e.g.* commercial colloid silver⁵⁰).

A change of structure that plays a part, formerly a little overrated, in colloid solutions with comparatively easily soluble particles is the growth of the larger particles at the expense of the smaller ones.⁵¹ In a suspension of calcium sulphate this change of structure is clearly visible, but in the more sparingly soluble barium sulphate the process goes on at an extremely slow rate.⁵² Formerly, aggregation, especially the irreversible process, was often interpreted as a recrystallisation. In irreversible aggregates as well as in compressed powders there gradually take place association and crystallisation phenomena which may greatly change the structure of the system (*e.g.* silver crystals in sediments from silver colloids).

Processes of the latter kind play a prominent part, especially in gelatinized colloids. On the whole a great variety of changes in structure and accompanying processes may occur in gels. When gradually deprived of water the gel of silicic acid, for instance, goes through a series of states, some of which differ rather decidedly from others.⁵³ The nature of these processes is not yet known. A gelatine gel probably consists of particles with a high percentage of "dry substance" and a liquid with a low percentage. In sol-formation water is supposed to pass over from the liquid to the particles, the particle-associations being thereby disintegrated; in the gel-formation the particles lose water.⁵⁴

In the study of the changes of structure and of the properties of secondary sols and gels we use, at least to some extent, the same methods as in the study of sols. Thus aggregation may be followed in the ultramicroscope, by sedimentation observations, by means of measuring the light-adsorption, the double refraction in magnetic and electric fields, the viscosity. The most reliable method consists,

of course, in direct countings of the particles in the ultramicroscope. But it is not always possible to carry out these countings. The viscosity is a very sensitive indicator of changes in structure, especially within the organic colloids. The values we arrive at when measuring the viscosity of an aggregating colloid are, however, dependent to a great extent on the state of current in the system and, consequently, on the kind of method employed for the measurement. The microscopic aggregation process is accompanied by a building up of a macroscopic network and the mechanical resisting power of this network determines, to a considerable degree, the viscosity measured by the experimenter. The aggregation may lead to the formation of secondary particles of a more or less high degree of dissymmetry. This can be studied by measuring the change which the double refraction of the sol in a magnetic field undergoes during the progress of aggregation.

The study of the structure of gels is a rather difficult one.⁵⁵ The particles of most gels do not contrast optically to any great extent with the surrounding medium and consequently the ultramicroscope is not able, as a rule, to make their primary particles visible.⁵⁶ Moreover, these are often packed together so closely that they cannot be distinguished from one another optically. On the other hand, we have been able to study with more success the macroscopic properties of the gels in chemical and physical respects. The elastic gels, especially gelatine, collodion, celluloid, rubber, &c., play a prominent part in industry and their investigation is therefore a matter of great importance.⁵⁷

With these few remarks concerning the structure of gels I must close my review. It is very incomplete—I am aware of the fact. The following discussion will, however, I am sure, fill up many of the blanks left open by me. In cases where our knowledge is still undeveloped, I trust the discussion will give valuable suggestions and help us to put the problems to new and crucial tests.

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Note on Prof. Svedberg's paper received from Prof. E. F. Burton (University of Toronto):—

It should be pointed out that Perrin's experiments on the variation of the distribution of colloidal particles with height were carried out for only very small heights and the resulting formula can be true only for a small distance near the surface. Substitution of the values of the constants in the equation—

$$n_2 = n_1 \cdot e^{-\frac{N}{RT} \cdot \frac{4}{3} \pi r^2 (s_1 - s_2) g (x_2 - x_1)}$$

with a value of, say, 25 cms. for $(x_2 - x_1)$, will show the unreality of the law for such distances. Perrin neglects altogether the mutual effect of the particles due to their charges.

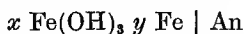
The following contribution to the General Discussion was received from **Dr. Wolfgang Pauli** (Vienna) in response to an invitation:—

THE GENERAL STRUCTURE OF COLLOIDS

BY

WOLFGANG PAULI

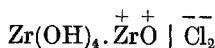
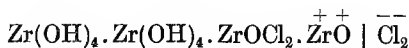
A careful physico-chemical analysis of ferric hydroxide sol, more particularly by means of potentiometric determination of the ion concentrations, had shown that it could, in the main, be considered as a complex salt of the composition—



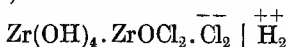
where "An" represents the anion of the ferric salt from which the sol had been prepared. From this structure the properties of ferric hydroxide sol may be deduced without any special assumptions and without introducing the concept of adsorption.

In the course of the last few years my collaborators, Mrs. Mona Adolf and Johann Matula, and myself have succeeded in extending the experiments to a number of oxy-salts and sols of polyvalent metals, and have thus arrived at a more general conception of colloids involving a more intimate connection with chemistry than has hitherto been possible.

To quote one example, a whole series of ionising complex molecules can be shown to exist in zirconium oxychloride (ZrOCl_2), by determining the H and Cl ion concentration (electrometrically), the conductivity, the freezing point and the transport numbers, of which I will mention a few only:

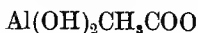


In addition to positive groups there occur also negative groups of a complex zirconic acid, such as—



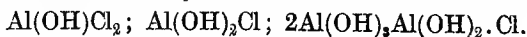
which can be combined with the above positive complexes.

The usual aluminium hydroxide sol, when prepared from aluminium acetate, proves to be an aluminium mono-acetate—



which is largely dissociated hydrolytically and in which the complex ions $3\text{Al(OH)}_3, \overset{+}{\text{Al(OH)}}_2 \mid \text{CH}_3\text{COO}^-$ have grouped themselves into colloid particles.

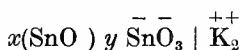
We have furthermore been able to prepare from AlCl_3 the following transitions to aluminium hydroxide sol—



In all cases the metal hydroxides show a tendency to transform themselves, by the addition of an ionogenic molecule, into charged particles, an aggregation of which forms the colloid complex.

We also demonstrated the interesting fact that, with increasing concentration of $\text{Al}(\text{OH})_3$, the aluminium oxy-salts incline to the formation of negative aluminate complexes, in addition to the positive ones. This tendency increases with increasing dilution, so that certain aluminium hydroxide sols stand at the boundary between positive and negative colloids. The occurrence of negative besides positive colloid complexes appears indeed to be a general phenomenon in metal oxide sols. We have proved it with certainty in the case of zirconium hydroxide sol, and made it very probable even in dilute ferric hydroxide sol. Thus a steady transition shows itself to the negative oxide sols.

The negative oxides also form colloid particles in accordance with the scheme shown for the positive oxide sols. Thus stannic acid—as suggested already by Zsigmondy—is peptized by alkali, through the agency of stannate ion, into colloidal stannic acid, which may be represented as



in complete analogy with ferric hydroxide sol.

The sols of the noble metals, *e.g.* the much-investigated gold sols, are to-day considered as minute particles of pure gold, which receive their charge by emitting gold ions into the solution. This view causes difficulties in answering even quite elementary questions. Why do the particles not aggregate further until complete precipitation takes place? How is it that the gold is precipitated on continued dialysis, since, if the above view holds good, it cannot lose its charge in this way? How is it possible to prevent the flocculation of gold sol during dialysis by the addition of a little ammonia to the external water, just as it can be prevented in the case of negative oxide sols by a little alkali, and of positive ones by traces of acid? Why is it impossible to prepare sols of the noble metals by electric dispersion in very clean vessels, *e.g.* of platinum, without the addition of alkali? Why cannot colloidal gold be amalgamated? Why does even the most energetic mechanical dispersion of pure mercury, according to Nordlund, not lead to sol formation?

All these and many other questions admit of unforced and satisfactory answers if we assume colloidal gold to be built up, not from particles of the pure metal, but from colloidal complex ions, in which the metallic particles receive their charge from a negative ion. Which is now the ionogenic molecule which furnishes these negative ions?

To answer this question we shall do well to examine, say, the preparation of gold sol according to Zsigmondy's method. It has been shown by Naumoff that the AuCl_4 first reacts with the K_2CO_3 present, with the formation of potassium aurate, KO_2Au , which we can consider as the salt of the auric acid, $\text{Au}^{\text{III}}.\text{O}.\text{OH}$. We have indeed satisfied ourselves that pure potassium aurate can be immediately reduced to red colloidal gold, *e.g.* by tannin, sugar, formaldehyde, and that even without any addition it is partly transformed into colloidal gold after a time. The reduction would have to proceed from the auri-compound *viâ* the auro-compound to pure gold. In this way, beside metallic gold, a mixed aurate of ter- and univalent gold is formed, to which our experience entitles us to

ascribe the magnificent red colour. Such a mixed compound has been prepared a long time ago, and that by no less a person than Berzelius. Berzelius found on analysing the purple of Cassius that the gold was present therein as Au_2O_3 , which he considered to be an auro-auric oxide. The mixture of Au_2O_3 and Au_2O indeed gives $2(\text{Au}_2\text{O}_3)$.

We will call these or analogous aurate mixtures "porphyrate complexes," and ascribe to colloidal gold a structure quite analogous to that of negative stannic acid and consisting of a series of gold particles to which are attached porphyrate ions, *e.g.* one of potassium porphyrate.

Viewed in this way, the contrast between Berzelius's strictly chemical and Zsigmondy's colloidal conception of the purple of Cassius disappears entirely. Berzelius prepared his purple directly from gold and tin salts; Zsigmondy was able to produce it from colloidal gold and colloidal stannic acid. In the second case analysis will show varying ratios of gold and stannic acid, whereas in the first case stoichiometric ratios may result.

Although the study of sols of the noble metals is still incomplete in many details, we wish to point out that the new conception leads to simple answers to the questions put above, and that it explains the colour of colloidal gold as absorption colour, and the colour change as due to a coating of the particles with the aurous oxide (purple to indigo), which has to be removed by rubbing to expose the metallic surface. We may therefore say generally that in sol formation the aggregation of the insoluble neutral particles does not proceed as far as precipitation, but that, while the particles are still small, the addition of an ionogenic molecule leads to the formation of a stable, ionized complex. In this process a certain relation between the molecules appears essential, which rests in the mentioned examples on the identity of the central atom.

The formation of colloidal salts of the alkalis and alkaline in media having a dielectric constant lower than that of water proceeds in an analogous manner. Here, on the one hand, association of the neutral molecules takes place (P. Walden), while, on the other, the small residue of ionizing molecules produces the charge. In the organic colloids matters are also similar. In albumin the chemically joined amino-acids represent a chain of neutral particles, which receives its charge from one of the ionizing amino-acids. Starch consists of a chain of amyloses, the ion causing the charge being probably that of amylophosphoric acid (M. Samec). Similar, the resin acid ion in certain resins, and the fatty acid ion in soaps, as suggested by McBain, may be considered as the charged portion of the colloid complex.

We venture to hope that the views set forth above have the advantage of leading to a more rigid uniformity in colloid chemistry and of establishing it more firmly between the modern physics of crystals, on the one hand, and the chemistry of complex salts, on the other.

Laboratory for Physico-Chemical Biology
of the University of Vienna.

SECTION I.—EMULSIONS AND EMULSIFICATION

Professor F. G. Donnan, C.B.E., F.R.S., opened the discussion in this section of the subject. The following is an abstract of his address :—

Emulsions may be defined as systems in which one liquid is dispersed in a second liquid in the form of small globules.

Dilute emulsions can be prepared by long-continued shaking of a pure hydro-carbon oil with pure water in a silica vessel. These emulsions often possess a high degree of stability, which must be ascribed to the influence of an electric double layer in preventing or hindering coalescence. Such emulsions possess all the characteristic properties of suspension colloids, though on a rougher scale. Investigations have shown that the interfacial potential difference and the corresponding stability of the emulsion are affected by positive and negative ions and by oppositely charged colloids in just the same manner as correspondingly charged suspension colloids.

Emulsification is greatly aided by the presence of a third substance, which forms a protecting film or membrane round the globules of the dispersed fluid. Such substances must always be used if it is desired to prepare emulsions of any considerable degree of concentration. Substances which lower the interfacial tension and therefore tend to concentrate at or in the interfacial layer, as, for example, the soaps, act as efficient emulsifiers. Many colloidal substances, such as gums, gelatine, etc., act as emulsifiers, and are largely used for this purpose in practical life.

Pickering has employed basic salts of copper, iron, etc., as emulsifying agents, and even such things as soot and lampblack have been successfully employed for this purpose in certain cases. The phenomena of interfacial adsorption and concentration, with the resulting formation of protecting films or membranes, play therefore a very important role in the formation and stabilisation of most emulsions, though the effects due to the electrical double layer and the differential adsorption of ions cannot be neglected.

It was thought at one time that the close packing of equal spheres would impose an upper limit to the amount of one liquid which could be emulsified in another. But this has been shown by later work not to be the case.

Very interesting phenomena occur when an emulsion "inverts," *i.e.*, when on the further addition of the dispersed liquid the latter exchanges its role with the liquid which has previously played the part of the continuous medium. This sudden change of type can be very readily detected by the sudden change of electrical resistance. When dealing with hydrocarbon and fatty oils emulsified in water by means of soaps, investigation has shown that electrolytes play an important part in determining the position of the inversion point and the nature of the liquid which forms the continuous medium. Thus di- and trivalent cations tend to render the oil the continuous phase, whilst univalent cations, and especially the alkali hydroxides, tend to cause the oil to be dispersed in a continuous aqueous phase. The physical factors which determine these phenomena are not yet completely elucidated.

The study of emulsions has thrown much light on the phenomena exhibited by colloidal systems, though the very much larger size of

the dispersed particles, and the correspondingly diminished Brownian motion in the case of even the finest emulsions, differentiate them in many important respects from colloidal solutions.

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EMULSION PROBLEMS IN MARGARINE MANUFACTURE

BY

WILLIAM CLAYTON, M.Sc.

Margarine is a substitute for butter, certain animal and vegetable oils and fats replacing butterfat. The oils and fats are liquefied together in certain proportions depending on the quality of the margarine required, and then churned with soured milk to form an emulsion. This emulsion is rapidly cooled, either by means of a spray of ice-cold water under pressure, or by flowing on to well-cooled revolving drums. The product in each case is then worked up by suitable kneading machinery to the required butter consistency and texture.

Margarine manufacture offers a splendid field for colloid research in several directions, but particularly in emulsions, both liquid and solid. Practically no published work appears on solid emulsions like butter and margarine, and as regards liquid emulsions, practice in margarine manufacture has followed empirical rules rather than definite physico-chemical conclusions.

The present discussion may conveniently include three main points in the making of a margarine emulsion:—

- (a) Factors depending on the degree and mode of agitation employed in mixing.
- (b) Factors depending on the animal and vegetable oils and fats used.
- (c) Factors depending on the water, milk, and other ingredients employed.

(a) FACTORS DEPENDING ON THE DEGREE AND MODE OF AGITATION EMPLOYED IN MIXING

The most essential factor in the production of a margarine of a butter-like texture, is the preparation of a stable and *suitably-phased* emulsion¹ containing from 77 per cent. to 84 per cent. fat and 23 per cent. to 16 per cent. water (milk serum). The milk used is at a temperature of about 7° C., and the melted mixture of oils and fats at about 40° C. Before actually chilling the emulsion its temperature is reduced to about 24° C., so that a thick custard-like emulsion ensues, of greatly enhanced stability. This greater stability is due to the viscosity of the system, and furnishes an instance where viscosity is desirable in emulsion preparation.² The object of chilling the emulsion is to fix the fine-grained condition arrived at, whereby the desirable intimate and finely-divided mixture is maintained in the solid state. Any "breaking" of the emulsion would lead to the formation of unemulsified fat, whereby the texture of the final product would be unsatisfactory.

Two types of emulsifying machines are in common use in margarine manufacture. The first is essentially a jacketed tank, permitting temperature control by circulating either hot or cold water. Milk is admitted to the tank, and then the oil mixture slowly run in, whilst constant agitation is maintained, *e.g.*, by means of rapidly-revolving baffle plates.

It is absolutely essential to run the oils into the milk, and not *vice-versa*.³ Thus a fine-grained emulsion results, of the oil-in-water type, which on cooling to 24° C. (with constant agitation) becomes remarkably permanent. The more slowly the oil is run in, the better the results obtained.

If on the other hand the oils be in the churn in bulk and the milk run in, an emulsion of the water-in-oil type ensues. The same thing happens if both phases are placed in bulk in the churn (say 80 per cent. oil and 20 per cent. milk) without undue mixing, and then the agitating device set in motion. On consideration of volume factors alone, it will be evident that if one has the oil phase in bulk and milk is introduced, stirring continually, the conditions from the purely mechanical aspect of disintegration of particles favour the formation of the water-in-oil type of emulsion. Such an emulsion is not "permanent." As soon as the agitation ceases, separation into layers occur, owing to the fact that the very nature of the emulsifying agents present, viz., milk colloids, demands the oppositely-phased system. Of course, this water-in-oil type emulsion can be "fixed" by any of the methods of rapid chilling used in margarine manufacture, but even then, the solid emulsion produced is far from satisfactory in the subsequent processes, and may well lead to a final margarine of poor texture.

The second type of emulsifying machine aims at the *continuous* production of emulsions, whereby there is economy in space, time, and power. The principle underlying continuous churns is the simultaneous admission of the oils and milk into a thermo-regulated chamber, whence, after some suitable device has ensured intimate mixing, an emulsion is discharged in a continuous stream.⁴ It is at once apparent that the same degree of freedom of the control of physical or mechanical factors is not permitted with this churn as with the older tank type. In my experience, even when using milk and oils, *i.e.*, when the purely *physico-chemical* conditions are satisfied, different *mechanical* treatments may lead to either the oil-in-water or water-in-oil type of emulsion. Sometimes, the passage through a continuous churn (wherein blades revolving 1,500 r.p.m. cause violent agitation) of a margarine emulsion of the oil-in-water type, will completely reverse the type of emulsion. Probably volume factors exercise a marked influence in such inversions.

It may be noted here that the nature of a margarine solid emulsion can be determined by staining with Sudan and examining under the microscope,⁵ or by extending Briggs's drop-method of dilution, by placing a small piece of the margarine in cottonseed oil at 15° C.; if the margarine is of the water-in-oil type, it slowly dissolves, if of the opposite type, it is unaffected. An electrical method was proposed by the author,⁷ based on the idea that though a small conductivity may result in an emulsion of the oil-in-water type, practically no conductivity would be observed in the case of a water-in-oil emulsion. That such a scheme is practicable has recently been shown by Sherrick⁸ and by Bhatnagar.⁹

The effects of different methods of agitation, and the degree of any one kind, on a mixture of oil and an aqueous phase, deserve far more attention than hitherto given. Undoubtedly one can both make and "break" an emulsion by agitation. Thus Sheppard,¹⁰ working on the emulsification of nitrobenzene in sulphuric acid, found that "de-emulsification was accelerated by slow shaking or even single vibration in some cases, for emulsions which remained stable

at rest, while shaking gently at a slightly higher frequency would re-emulsify to a system again stable at rest." The influence of vibration on emulsions has been noted by Ayres,¹¹ and he mentions an instance where an emulsion, so stable as to defy separation in a centrifuge, was de-emulsified by the vibration attendant upon its transport in an express railway train.

The prevalent idea regarding emulsification in general, and margarine churning in particular, is to agitate the mixture of milk and oils as violently as possible. Such agitation, it has been argued, results in the formation of very small globules, a most desirable feature in a stable emulsion. Consequently an empirical limit only is set on the degree of stirring up an emulsion. For any given type of emulsifying machine, it seems reasonable to believe that an optimum degree of agitation is possible, favouring a very stable system.

Shaking is an inferior method of making emulsions, because as the emulsion becomes more perfect, the smashing action between the relatively heavy and light particles becomes more feeble, whereas the smashing forces should be increased. Briggs¹² has recently shown that "intermittent shaking was vastly more effective than uninterrupted agitation," and that "intermittent shaking may be six hundred or even a thousand times more effective than uninterrupted but equally violent agitation." From his results, it would appear that the ideal process of emulsification is one wherein the dispersed phase is as completely disintegrated as possible, whilst the continuous medium is left as far as possible unbroken. It seems to me that continuous shaking would give equally as good results as the intermittent shaking, provided the emulsified portions of the mixture are continually removed from the mass so that the energy of shaking is concentrated on the remainder.

(b) FACTORS DEPENDING ON THE ANIMAL AND VEGETABLE OILS AND FATS USED

The solid fats used in margarine manufacture include stearine (M.Pt. = 50° C.), beef-jus (48° C.), oleo (30° C.), lard (33° C.), palm-kernel oil (28° C.), and coconut oil (25° C.), whilst the liquid oils include cottonseed, arachis, soya, rape, sesame, etc. A margarine mixture may include from three to six of these ingredients, so proportioned as to give a melting-point of about 26° C.¹³

Experiments have been made to inquire whether these various ingredients were alike in their capacity of being emulsified, or whether by a suitable choice of oils and fats, a margarine mixture could be obtained which would with greater ease give an emulsion of more than the usual stability. Using the Donnan drop-pipette, numerous drop number determinations were made of various oils and fats against water at various temperatures.

The first point observed was the fact that only a small difference in drop numbers exists for these oils and fats, *e.g.*, at 35° C. against pure water, the following numbers were repeatedly observed:—

Palm kernel oil	= 74	lard	= 59
butterfat	= 71	oleo	= 66
cottonseed oil	= 65	arachis oil	= 66
coconut oil	= 61	soya bean oil	= 68

The effect of the free-fatty acids in edible oils is small. Thus no change in drop number was given by various samples of the liquid oils, with free fatty acid contents ranging from 0.05 per cent. (as

oleic acid) to 0.5 per cent., the figures usually found. The coconut oils and palm-kernel oils investigated had free fatty acid contents of 0.05 per cent. to 0.08 per cent. (as lauric acid). A coconut oil not so well refined as the usual edible oil employed in margarine, and possessing a distinct odour of coconut, had 1.85 per cent. of free lauric acid, and the drop number at 35° C. was 73 instead of the usual figure 61.

Temperature has no pronounced influence on the interfacial tension, an observation agreeing with the results of Meunier and Maury,¹⁴ though they used oils very different to mine.

Effect of Temperature on Drop Number

Arachis Oil-water.	Cottonseed Oil-water.	Coconut Oil-water.	
25.5° C. = 66 drops.	27.5° C. = 65.	30° C. = 69.	
46.0° C. = 65 drops.	35.0° C. = 65.	35.0 = 61.	
50.0° C. = 64.5 drops.	50.0° C. = 63.	50.0 = 65.	
Palm Kernel Oil-water.	Soya Bean Oil-water.	Lard- water.	Oleo- water.
30° C. = 73	35° C. = 68	35° C. = 59	35° C. = 66
35° C. = 74	50° C. = 68.5	50° C. = 66	50° C. = 69
50° C. = 61			

Tap water gave results practically identical with distilled water.

(c) FACTORS DEPENDING ON THE WATER, MILK, AND OTHER INGREDIENTS EMPLOYED

It is the practice to add salt to margarine during the final stage of blending. In the use of the author's invention,¹⁵ of a machine for the continuous production of margarine, the salt is added in solution in the milk during emulsification. Drop number determinations have shown that NaCl promotes the dispersion of oils and fats in water. For example, at 35° C:—

Coconut Oil in :			Butterfat in :		
Water	= 61	drops.	Water	= 71	drops.
1 per cent. NaCl	= 65.5	"	1 per cent. NaCl	= 80	"
2 " "	= 70	"	2 " "	= 84.5	"
3 " "	= 74	"	3 " "	= 87.5	"

At 13 per cent. NaCl concentration (the concentration of the salt present in the aqueous phase of the total emulsion) no drop numbers were determined, because of sausage-like formations of the drops.

The explanation as to why NaCl, which will "break" emulsions of oil in (say) soap solution, facilitates dispersion in pure water, seems to be that by preferential adsorption of the Cl ion at the oil-water interface, caustic soda is formed which unites with the free fatty acids present in the oil, and so forms a soap. Thus two coconut oils were examined at 35° C. One had 0.07 per cent. free fatty acid, the other 1.85 per cent. In a 1 per cent. NaCl solution they gave drop numbers of 65.5 and 79 respectively. Actual tests on a works scale have shown that salt (2 per cent. concentration on the total margarine, 13 per cent. concentration in the aqueous phase) does facilitate emulsification.

Emulsifying agents are frequently added to the milk or oil in margarine manufacture, and numerous patents for such additions exist, *e.g.*, egg-yolk, lecithin, gelatin, glycerin, albumin, etc. Gelatin is an excellent emulsifier. A palm kernel oil giving a drop number of 73 in water in 30° C. gave 120 drops in 1 per cent. gelatine. Two samples of oils at 25° C. gave the following results:—

Cottonseed Oil in :			Arachis Oil in :		
Water		66 drops.	Water		66 drops.
0.25 per cent. gelatine	124	„	0.5 per cent. gelatine	140	„
0.50 „ „	137	„	1.0 „ „	148	„
1.0 „ „	143	„	2.0 „ „	155	„
2.0 „ „	149	„	3.0 „ „	163	„
3.0 „ „	149.5	„			
4.0 „ „	150.0	„			

The curve given by plotting the results for cottonseed oil suggests a maximum effect at about 3 per cent., but this question demands further inquiry.¹⁶

It is now evident that extensive investigations require to be made before a thorough account of a margarine emulsion is complete. It is probably the most complex emulsion system in industrial practice. The oils and fats are not emulsified with water only (except in special cases, *e.g.*, “pastry margarines”) but with milk, and this milk has been artificially soured by the action of lactic acid bacterial. In the milk there is lactic acid, milk colloids, lactose and solid clots of casein. What the effects of these substances are on the emulsion is a field for further research.

Preliminary measurements indicate that lactic acid has a slight positive dispersing effect and lactose a more pronounced effect. Thus a coconut oil giving a drop number of 69 in water at 30° C. gave a drop number of 116 in 1 per cent. lactose. In three separate solutions of lactose, coconut oil gave 116, 118 and 116 drops. Such a result is quite unexpected, and is receiving further investigation.

In conclusion, I take this opportunity of thanking Calder's Margarine Co., Ltd. (Liverpool), for affording me every facility to carry out these experiments.

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REVERSAL OF PHASES IN EMULSIONS AND PRECIPITATION OF SUSPENSIDS BY ELECTROLYTES : AN ANALOGY

BY

SHANTI SWARUPA BHATNAGAR

Donnan pointed out the resemblance between emulsions and colloidal solutions as early as 1899 (cf. *Zeit. Phys. Chem.* **31**, 42, 1899). Further work carried out by Ellis (*Zeit. Phys. Chem.*, **78**, 321, 1911) and by Lewis (*Zeit. Kolloid Chem.*, **4**, 211, 1909) has established that neutral oil emulsions behave like model suspension colloids. The investigations of Hatschek on the influence of electrolytes on emulsions, in which the disperse phase and the continuous medium were of equal densities (*Zeit. Kolloid*, **9**, 159, 1911), pointed out the resemblance still further. It was, however, found that neutral oil emulsions were not particularly sensitive to the effect of electrolytes.

There has been some hesitation on the part of various investigators on emulsions in advocating the study of the effects of electrolytes on soap emulsions because they are not free from electrolytes. As far as the author is aware, the only work in this field is a paper by Clowes (*J. Physical Chem.*, **20**, 445, 1916). His work is, however, restricted to a particular type of emulsion only, and the accuracy of the quantitative data obtained by him is, in his own words, "rough at best," because of the difficulties in determining accurately and sharply the point when an emulsion of oil-in-water changes into one of water-in-oil under the influence of electrolytes.

There are two methods generally in use to determine the type of the emulsion, namely, the "colour-indicator" method of Robertson and the drop-method of Briggs. In the colour-indicator method of Robertson, use is made of some oil soluble dye like Sudan III. In an emulsion of oil-in-water, this colour remains confined to the particles of oil which exist as globules, but in an emulsion of water-in-oil the colour spreads over the whole surface of the continuous phase and the microscopical examination reveals the type of the emulsion under consideration.

This method has been found unsatisfactory by Newman (*Z. Physikal. Chem.*, **18**, 34, 1914), and it is also likely that the character and stability of an emulsion might be disturbed by the introduction into the system of a foreign substance like Sudan III., and thus vitiate the accuracy of the quantitative data. That such doubts are justified is abundantly clear from the observations of Clowes (*J. Physical Chem.*, **20**, 445, 1916), who finds that organic impurities have an appreciable effect on the size of globules in emulsions.

The drop-method of Briggs is based on the principle that an emulsion can be diluted by adding more of the continuous medium, but not by adding excess of the disperse phase. This method suffers a disadvantage on account of the fact that a single drop of an emulsion may not always represent the emulsion, whilst if a representative portion of an emulsion is shaken with a large quantity of oil or water, the temporary emulsion due to mere mechanical shaking may make it extremely difficult to determine the type.

Besides the defects pointed out above, these methods completely fail to give a sharp indication of the critical point, and are, therefore,

not convenient for studying the effects of electrolytes and other substances on emulsions. In order to obtain a correct quantitative data on the effect of electrolytes on emulsions of soap solution and oil, an electrical method was employed which has been described in detail in a paper contributed by the author to the Chemical Society (*J.C.S.*, **117**, 542, 1920).

The principle of this method is based on the fact that an emulsion of oil-in-water type, specially when soap solutions are used, undergoes a sudden drop in electrical conductivity at the point when it changes into the reverse type under the influence of electrolytes.

The procedure of using alkaline solutions and free fatty acids in the oil employed by Clowes has been found unsatisfactory for repeating observations. When dilute solutions of alkalis are used, a comparatively large amount of free fatty acid in the system is left unneutralised. The presence of free fatty acid or alkali makes the system more complex. Besides, alkali and acids have been found to have definite effects on the degree of dispersion in emulsions. In order to obtain consistent and comparable results, various pure soap solutions were employed.

It is to be noted here that very special precautions have to be observed in ensuring identical conditions of shaking, form and size of the vessels, &c. used (cf. *J.C.S.*, **117**, 542, 1920). A large number of electrolytes was examined, and the detailed results obtained have been recently communicated in a paper to the Chemical Society. Two representative tables of results are shown below.

Experiments with Electrolytes

Volume of oil phase = 10 cc.

Volume of aqueous phase = 10 cc.

R = inversion point.

TABLE 1
(*Soap Potassium Oleate.*)

Amount of Soap, in millimols at R.	Barium Nitrate, in millimols at R.	Ca(NO ₃) ₂ in millimols at R.	Amount of Pb(NO ₃) ₂ , in millimols at R.	Cr ₂ (SO ₄) ₃ , in millimols at R.	Al ₂ (SO ₄) ₃ , in millimols at R.
0.080	2 × 0.0199	2 × 0.020	2 × 0.0198	0.017	0.014
0.10	2 × 0.0251	2 × 0.027	2 × 0.0252	0.019	0.017
0.151	2 × 0.041	2 × 0.042	2 × 0.04	0.028	0.025
0.162	2 × 0.044	2 × 0.044	2 × 0.044	0.03	0.027

TABLE 2
(*Soap Sodium Stearate.*)

Amount of Soap, in millimols, at R.	Ca(NO ₃) ₂ , in millimols at R.	Al ₂ (SO ₄) ₃ , in millimols at R.	Cr ₂ (SO ₄) ₃ , in millimols at R.	Ba(NO ₃) ₂	Ca(NO ₃) ₂	Pb(NO ₃) ₂
0.09	0.040	0.015	0.016	0.0398	0.040	0.0396
0.12	0.056	0.020	0.023	0.0502	0.054	3.0504
0.16	0.090	0.028	0.029	0.082	0.084	0.08
0.2	0.10	0.03	0.032	0.088	0.088	0.088

TABLE 3

Data of As₂ S₃ sols by Mukherjee, J. Amer. Chem. Soc., 37, 2030, 1915.

Lith. Chloride concentration.	Time for perceptible Change.	Alum. Sulph. concentration.	Time for perceptible Change.
N/10	7 minutes	N/2000	9 minutes.
N/9	5 minutes	N/10000	Less than a minute.
N/8	3 minutes	—	—
N/7	Few seconds	N/9000	Five seconds.
Barium chloride	—	—	—
N/700	15 minutes	—	—
N/600	Few seconds	—	—

TABLE 4

Order of precipitating Power of Cations for various Suspensoid Systems.

- ¹ Gold.—Al>Ba,Sr>Ca>Na>H>Cs>Rb>K>Na>Li
- ² Platinum.—Al,Pb>Ba>K>Na
- ³ Copper Ferrocyanide.—Al>Ba>H>Cs>Rb>K>Na>Li
- ⁴ Prussian Blue.—Fe,Cr,Al>Ba>H>Cs>Rb>K>Na>Li.
- ⁵ Silver.—Al>Ba,Sr,Ca>H>Cs>Rb>K>Na>Li

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- ³ and ⁴ Pappada, *Koll. Zeitsch.*, 1910, **6**, 83; 1911, **9**, 136.
- ⁵ Pappada, *Gaz. Chim.*, 1912, **42**, I, 263.

The results shown in Tables 1, 2 indicate in a marked manner the differences in the amounts of various electrolytes required to bring about the reversal of phases. Tables 3 and 4 are the data obtained for precipitation of gold, arsenious sulphide, and other sols by electrolytes. The effect of the valency of the electrolyte is worth noting. In both cases the trivalent electrolytes have a greater effect than bivalent ones. The power of reversing the phases in these electrolytes is in the order Al>Cr>Nickel>Lead>Barium>Strontium and Ca. It is interesting to note that, in many suspensoid sols also, the same order persists under different conditions. The author has investigated various soaps, and although the amount of electrolytes required to bring about the reversal of phases differs with different soaps, the valency effect of the electrolyte and the order still holds good.

EFFECT OF DILUTION ON THE REVERSAL OF PHASES BY
ELECTROLYTES

In order to examine still more closely the parallelism between the reversal of phases in emulsions and the precipitation of suspensoids by electrolytes, it was considered desirable to investigate the effect of dilution on the stability of emulsions. The effect of dilution on the precipitation of suspensoids by electrolytes has been studied by Woodstraw, Mukherjee, and theoretically by Smoluchowski. The table of results shown below indicates the change in the rate of coagulation on dilution (Mukherjee and Sen, 115, 464, 1919, *J.C.S.*).

TABLE 5

Sol A contained 17.58 millimoles of arsenious sulphide per litre. Sol B was prepared by diluting sol A five times, and sol C by diluting sol A ten times, with pure water.

Electrolyte : lithium chloride

Dilution (after mixing).	Sol A.	Sol B.	Sol C.
5N/16	—	—	Coagulation after 20 seconds.
5N/32	—	Coagulation after 30 seconds.	Coagulation after 50 seconds.
N/8	Instantaneous coagulation.	Coagulation after half an hour.	Perceptible change after 8 minutes. Coagulation after 2½ hours.
N/16	Change perceptible on mixing. Coagulation not observed after 1½ hours.	Change just after mixing not perceptible.	Change perceptible after 45 minutes.

The results obtained for emulsions also point to the fact that the greater the dilution or the distance between the oil particles in an emulsion, the larger the amount of the polyvalent electrolyte required to bring about the reversal of phases. These results indicate a parallelism between the reversal of phases and the precipitation of suspensoids by electrolytes. A few observations were also made to see how the rate of coagulation of the typical natural emulsion, milk, is affected by dilution. The following table shows some of the results obtained.

TABLE 6

Vol. Solution always 20 c.cs.	Time for First perceptible Change on the addition of a known amount of H_2SO_4 .
Pure milk -	Immediately after adding.
Twice diluted -	9 minutes 2 seconds.
Thrice diluted -	12 minutes.
Four times diluted -	15 minutes 3 seconds.

It is thus evident that even in the case of milk, the greater the dilution the stronger is the acid required to bring about an immediate perceptible coagulation change. The fact that the quantitative results in case of reversal are not of the same order as in precipitation of colloids, indicates that, besides the electrical change in the film surrounding the globules, some chemical change also takes place. The nature of the film can be changed chemically, or electrically, e.g., $\text{Fe}(\text{OH})_3$ reverses the type, perhaps by merely changing the charge on the protective sol. A protective sol which is positively charged tends to stabilise, as water in oil emulsion. All negatively charged protective colloids, like sodium oleate, gelatine, casein, etc., form oil in water emulsions. Electrolytes like $\text{Ba}(\text{NO}_3)_2$, AlCl_3 , etc., form bivalent and trivalent soaps which are positively charged and, therefore, change the type of the emulsion.

A complete study of the effects of electrolytes, the degree of dispersion, and the distance between the particles in these emulsions, points to the conclusion that the character of emulsions as model suspension colloids is not destroyed by using soap solutions as stabilising agents, and that the latter may be regarded merely as protective colloids. The theoretical interest arising out of the problem is great. The observed parallelism between the reversal of phases in emulsions, and the precipitation of colloid sols in suspensions, suggests that the cause or causes operating to produce such identical effects may also be identical. A thorough study of emulsions and a comparison of the large amount of data already obtained on simple and well-studied colloidal sols (like gold, As_2S_3 , and blood, etc.) in the light of a possible parallelism between them, may lead one day to the clearing up of the mystery of coagulation and prepare a way for a rational theory of colloidal solutions and emulsification.

Apart from the theoretical interest of the problem, a thorough study of the effects of electrolytes on the stability of soap emulsions is likely to be of great practical value. For example, the differences in the amount of electrolytes required to bring about the reversal of phases with different soaps points to the probability of a difference in their protective actions.

The results obtained for B.P. paraffin oil indicate that the soaps can be arranged in order of their protective action as Pot. Stearate > Sod. Stearate > Sod. and Pot. Palmitate > Pot. Oleate > Sod. Oleate. The results have an important bearing on the washing power of soaps. Provided the water is free from electrolytes, the cleansing power of these soaps may also be in the same order. The old hypothesis of Chevrueil that the cleansing power of soap is due to the free alkali liberated is now discarded in the light of recent extensive investigations of MacBain (*J. Soc. Chem. Ind.*, **37**, 249 T, 1918). According to the modern conception the washing power of soap is due to its emulsifying efficiency, or, better, to its protective action, which keeps the dirt and grease bound in the form of an emulsion. A complete investigation of the emulsifying efficiency of various soaps for the more common dirt, like dust, soot and grease, will be of very great practical importance for the soap industry. On this view, the cleansing properties of soaps should be considerably affected by the electrolytic impurities in water, and traces of Ca, Barium, and trivalent salts will be injurious for cleansing purposes, as they would tend to form a water-in-oil emulsion which is sticky and difficult to be washed with excess of water. My best thanks are due to Professor Donnan for his kind advice and assistance.

PHYSICAL CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE,
LONDON.

DISCUSSION

Prof. H. R. Procter : I do not wish to criticise anything that has been said, but merely to add a small fact which has come to my knowledge, and which may be of interest to some people who have been engaged in the subject. We have been making experiments in my laboratory upon the surface tension lowering of solutions of sulphonated oils. That is a practical question in the leather trade, and also has general bearings. We have been making these experiments by the ordinary method of dropping a mineral oil below the surface of a solution of sulphonated oil, and we find that the surface tension is largely dependent upon the exact hydrion concentration. It rises steadily with increasing hydrion concentration up to a certain point, at which it reaches a maximum and then begins to diminish, so that there is a point somewhere between the alkalinity and acidity, a point in the wide region between the colour change of methyl orange and the colour change of phenolphthalein, at which the surface tension in this particular case is at a maximum.

Mr. E. Hatschek : I think that Mr. Bhatnagar's parallel between the reversal of phases in emulsions and the precipitation of suspensoids by electrolytes may be questioned, and there may be an alternative explanation. What the thing really turns on is the relative solubility of the fatty acid salt formed in water and in oil. The fatty acid salts of the tri- and some bi-valent cations are soluble in oil, while those of the univalent ones are soluble in water. If a film of oil-soluble soap is substituted for the film of water-soluble soap, it seems to me that reversal of the phases would naturally follow, provided both are present in sufficient amount. In this point, too, the parallel with suspensoids fails, as none exist in which the phase ratio even remotely approaches 1 : 1.

Prof. J. W. McBain : The results obtained by Mr. Bhatnagar show no parallelism between protective action and solubility of the soaps in aqueous phase. I have no knowledge of the relative solubilities in oil of the soaps examined; perhaps someone else has that information.

Prof. W. C. McLewis : I was particularly interested in one point Prof. Donnan raised, namely, that one could get a stable emulsion with two absolutely pure phases. I would like to ask Prof. Donnan for a little more information on that point, because I have got an idea that ultimately the stability will depend upon the presence of at least one further substance. Of course, in the case which Prof. Donnan cited, oil and water, under conditions in which the oil and water were extremely pure, you cannot avoid having the ions of water there, and I would like to know if his idea is that, even in that case, the ions would be the stabilisers. Another point with regard to emulsions in general: emulsions can be de-emulsified by the ions of electrolytes, and the de-emulsifying action depends upon the valency. Hitherto, of course, comparisons have been drawn in terms of concentration, *i.e.*, we have compared the de-emulsifying powers of various electrolytes of the same concentration, but the

idea which suggests itself to me is that we should compare electrolytes not at the same concentration, but at the same thermo-dynamic activity. I will not go into the question of thermo-dynamic activity, but, as you know, it has thrown a great deal of light on many other problems, and it seems to me that it is quite probable that work in other fields dealing with the measurement of thermo-dynamic activity of various ions might, if brought into the field of emulsions and of colloidal solutions, tend towards a revision of our knowledge as regards both coagulative and protective effects. There is one other point, and it is one raised by Mr. Clayton and one he would have dealt with had he been here. Nearly all emulsions and colloidal solutions are electrically charged and, as a rule, the ions with the opposite charge have a coagulating power. Mr. Clayton, however, considers that he has found a case in which a suspension can be coagulated by a colloid of the same electrical sign. If this is really the case, the observation becomes one of the greatest importance as it certainly would diminish greatly the value of the so-called electrical view of stability of dispersed systems. It has always been a moot point as to how far we should consider such phenomena as electrical or as capillary. Probably, ultimately we shall have to bring in both effects though, of course, that helps us very little at the present time, in view of the fact that the theory of electro-capillarity is so very little developed. In connection with Mr. Clayton's observation, I would draw your attention to the behaviour of a benzene emulsion. You can make an emulsion of benzene in water containing a very little gelatine and obtain a highly concentrated emulsion. The benzene is

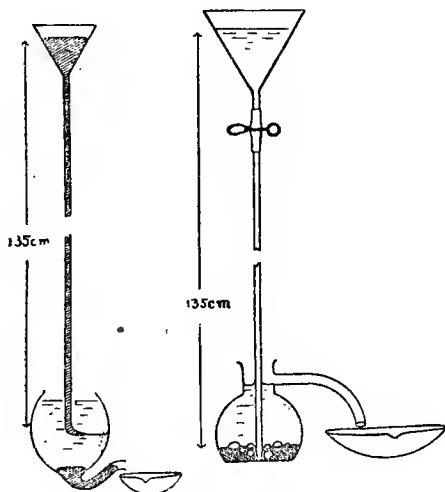


FIG. 1.

FIG. 2.

the disperse phase. Further, it can be shown that the benzene particles are negatively charged. This emulsion can be de-emulsified by hydrogen ion, and also by hydroxy ion. The effect of the hydrogen ion is to be expected; that of the hydroxyl ion is quite unexpected. In this case, however, the paradox is easily explained. What happens probably is that the caustic soda attacks the protecting gelatine, and the emulsion becomes de-emulsified by removal of the stabiliser and not by a direct action of the hydroxyl ion. How far other anomalies might be brought into line is an open question.

Dr. T. Svedberg : I should like to call attention to a special case in the emulsifying of mercury. The rather striking experience was made by a friend of mine, Dr. I. Nordlund, at Upsala. This experiment is of interest because it shows that there are two different methods of preparing emulsions of substances that have a very high surface tension. If mercury is pressed through a glass tube into water in form of a fine jet striking against a glass wall (Fig. 1), you get a mercury-water emulsion with rather coarse particles. On the contrary, if you press water through the mercury (Fig. 2), there are formed, as the water bubbles rise to the surface, thin membranes of mercury, and these lamellæ when bursting produce very fine particles. Thus a real, though very diluted, mercury hydrosol, pale yellowish-brown in colour, is obtained. In order to prevent coagulation and maintain the primary structure, a trace of potassium citrate should be added to the water (suitable concentration : 0.0025 normal).¹ I have repeated the experiment with oil and water, but in this case no difference was found between the products obtained by the two procedures.

Prof. Procter : With regard to Mr. Bhatnagar's paper, there is an extraordinary similarity between the structure he describes and the structure of connective tissue. The connective tissue consists of fibres, made up of small fibrils of about $1\ \mu$ in diameter, parallel to each other, and apparently these are not living cells. They have no nuclei, but seem to be produced by the cells which exist among them, and which possibly move along the fibres.

¹ *Koll-Zeitschr.*, 26, 121, 1920.

SECTION II.—THE PHYSICAL PROPERTIES OF ELASTIC GELS

The Introductory Paper to this Section of the Discussion was given by Mr. Emil Hatschek.

THE PROPERTIES OF ELASTIC GELS

BY

EMIL HATSCHEK, F.INST.P.

The statement that the familiar table jellies (gelatine gel) are typical representatives of the class to be discussed in the present paper will probably, at the outset, be found more useful than an attempt at strict definition. These systems exhibit immediately two of the most characteristic properties of the elastic gel: stability of shape, notwithstanding a very high content of liquid (about 95 per cent. in the case quoted) and perfect elasticity within certain narrow limits.

The gel may be obtained in two opposite ways: either by transformation—which may be reversible or irreversible—of a sol, *e.g.*, by cooling a gelatin sol below a certain temperature; or by allowing the dry substance to “swell” in an appropriate liquid. Practically all substances from which elastic gels may be produced show this capacity of swelling, though to an extent which differs widely. Only certain liquids will cause a given substance to swell, and the relations between the constitution of the solid and the liquid, on which this property is based, are at present quite obscure. Thus gelatine and agar (the former a protein, the latter a mixture of carbohydrates) swell in water at ordinary temperature, but do not dissolve until the temperature is raised. Vulcanised india-rubber swells in various organic solvents such as benzene, toluene or xylene, without dissolving. Finally, the processes of swelling and dispersion or solution may proceed *pari passu*, as with gum arabic at ordinary temperature. At low temperature, a definite stage of swelling may be observed to precede solution.

The elastic gel which can be most easily reproduced and has, accordingly, been studied most frequently and extensively, is that of gelatine. Bodies of any desired shape can be obtained by pouring the gelatine sol into suitable moulds and allowing it to set for a period of not less than 24 hours (*cf. infra*, E. Fraas). The procedure, once chosen, must be rigidly adhered to throughout, since all the properties of a gel depend, not only on its composition, but also to a marked extent on its history, especially its “thermal history,” *i.e.*, the temperatures to which the sol has been exposed and the duration of such exposure. Some of the principal investigations will now be briefly summarised.

ELASTIC PROPERTIES .

These have been studied principally by R. Maurer,¹ P. v. Bjerken,² E. Fraas,³ and A. Leick.⁴ All these investigations date back some time, and were undertaken with a view to studying a material with very low modulus and sufficiently transparent for examination in polarised light, rather than with the intention of elucidating such

problems as the structure of gels. Both Maurer and Leick determined Poisson's ratio for gels of various concentrations and find it 0.5 within the limits of error—a result which is not surprising in view of the large percentage of liquid. Maurer studied the elongation of gel cylinders of considerable diameter (2.21 cm.) with small loads, the extensions being measured microscopically. His figures for the modulus are in good agreement with those found by Leick, which range from 2.42 (gm/mm²) for 10 per cent. to 29.4 for 45 per cent. gels. Leick found the modulus E roughly proportional to the *square* of the gelatine concentration; the ratio E/c^2 , however, varies somewhat irregularly, and decreases with increasing c . All the investigators find that the modulus increases with increasing load.

Fraas studied the ageing of gels and found that a constant modulus was not reached until about 24 hours after apparently complete setting. These hysteresis effects are universal in colloidal systems, and the increasing modulus of a gel is paralleled by the increasing viscosity of the sol, when kept at a temperature above the setting point. In the following table one series of Fraas's results is given to illustrate the magnitude of the effect.

Cylinder of 20 per cent. Gelatine Gel

Hours after removal from mould	-	1	2	3	4	5	6	7	24
Extension produced by 50 gm. weight		12.5	7.5	7	7	6.5	6.5	6	5

Maurer, and more particularly Leick, also studied the effect of various substances dissolved in the water on the elastic modulus of gelatine gels; the results are of particular interest from the colloidal point of view, inasmuch as they can be co-ordinated with the well-known effects of such solutes on other properties of the system, *e.g.*, maximum swelling, setting point of sol, &c. Leick finds that the addition of various chlorides lowers the modulus, sodium sulphate is without action, while cane sugar and glycerine raise the modulus considerably. Chlorides also lower the viscosity and setting temperature of the *sol*, while glycerine and cane sugar (generally substances containing hydroxyl groups) raise both constants.

The elasticity of gels is perfect only for small loads applied for a short time, but very little work has been done on relaxation in such systems. A. O. Rankine⁵ maintained gelatine gels of low concentrations (3.4 to 4.5 per cent.) at constant strain and plotted the stress necessary to do this against time. The stress, within the limits of concentration and time investigated, never becomes zero. Breaks occur in the time-stress curves, which are taken to indicate that the elastic limit has been reached. The concentrations employed by Rankine are very much lower than those at which determinations of the modulus, &c. have been made.

Reiger⁶ determined the relaxation time of gelatine gels by optical means (disappearance of the double refraction produced by strain). The investigation was undertaken with the object of testing Maxwell's relation between modulus, viscosity and relaxation time, and was accordingly carried out at 29° C., *i.e.*, at a temperature very near the "melting point" of the gel. In these conditions Reiger found a relaxation time of 10 minutes for 20 per cent., and about 41 minutes for 40 per cent. gel.

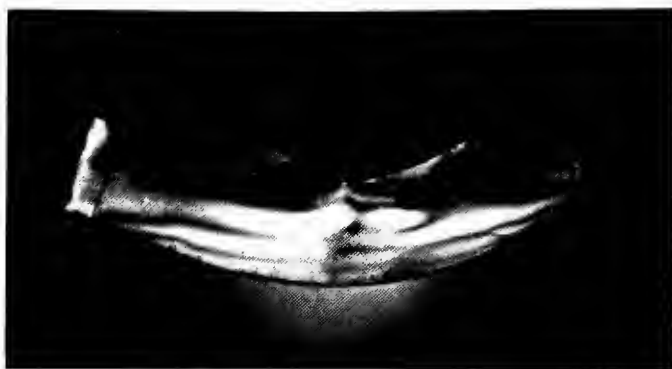


FIG. 1.

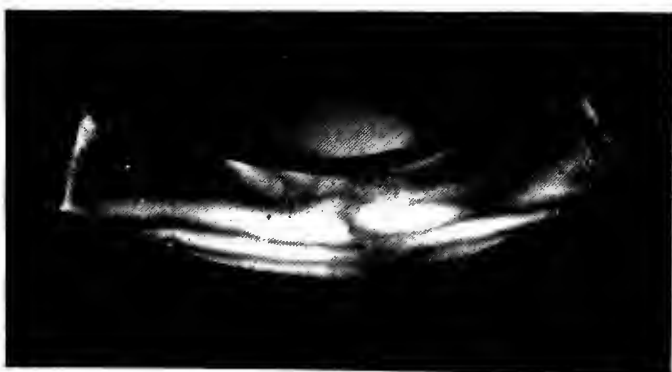


FIG. 2.

That the conditions are entirely different at lower temperatures is shown by experiments by the writer, published here for the first time. Rectangular prisms of gelatine gel (10 per cent.) with 1 per cent. of sodium fluoride, to prevent putrefaction, were cast and allowed to set for 36 hours before removal from the mould. One of these prisms was then bent between three stops fixed on a glass plate, the latter being covered with paraffin oil to prevent adhesion of the gel and consequent irregular deformation. The specimen was then photographed in polarised light (double plate glass as polariser, Nicol as analyser) within 10 minutes of the application of stress at room temperature, about 15° C. This photograph is shown in Fig. 1. The glass plate with the specimen was then placed in a moist chamber for five days, being examined at intervals (visually) without any noticeable change showing itself. At the end of five days the stress had practically disappeared, so that the specimen could be removed without friction and without straightening itself appreciably. It was then again placed on an oiled glass plate and photographed as before, the result being shown in Fig. 2. Considering the extreme sensitiveness of 10 per cent. gel to deformation, it may be said that the appearance is substantially unaltered, and that at any rate the optical anisotropy caused by strain has not disappeared with the removal of the stress. The absence of relaxation in a system consisting to about 90 per cent. of liquid is certainly remarkable and will be referred to again.

OPTICAL PROPERTIES

The double refraction produced by deformation has been referred to incidentally in the preceding paragraph. Quantitative investigation of this property has been carried out chiefly by Leick (*l.c.*). His principal results (obtained with gel plates in tension) are: (1) the double refraction ($D = n_e - n_o$) is, *cæteris paribus*, very approximately proportional to the strain, and (2) for equal relative elongations the double refraction is roughly proportional to the gelatin content.

The refractive index of both gelatine sols and gels has been shown by G. S. Walpole⁷ to be a linear function of the gelatine concentration. If the refractive index is plotted against the temperature over a range containing the setting point, no discontinuity occurs at the latter, *i.e.*, when the sol is transformed into gel.

On the whole, our knowledge of the elastic and the related optical properties of gels must be pronounced slight. As in other branches of the subject, non-aqueous systems have received hardly any attention; their study is eminently desirable, as the enormous complications introduced in the case of a protein like gelatine by the formation of salts, and their electrolytic and hydrolytic dissociation, would be absent. There is a very large literature on the stress-elongation curve of india-rubber, which, however, refers only to the dry material and is not of immediate interest. The writer has found only one reference to a rubber gel in a paper by A. E. Lundal,⁸ who determined the tensile modulus of rubber which had imbibed 133 per cent. of paraffin oil and found it about one-half that of the dry material.

DIFFUSION IN GELS

This phenomenon has, for various obvious reasons, received a considerable amount of attention. Thos. Graham already used dilute gels instead of pure aqueous solutions in the study of diffusion, and found the rate approximately the same in both. This, however, only holds good of gelatine gels up to, say, 3 or 4 per cent. and agar gels

under 1 per cent. In more concentrated gels the rate of diffusion decreases markedly with the concentration, but no quantitative relations have, so far, been determined. The rate of diffusion for a given solution and gel concentration can be affected by various solutes in the latter. Among the earliest investigations on the point are those of H. Bechhold and J. Ziegler⁹, who found NaCl and NaI without effect; Na_2SO_4 and several non-electrolytes as dextrose, glycerin and alcohol reduced the rate of diffusion of certain solutes. A certain—though not exact—parallelism shows itself between the effect of solutes on the elastic modulus and the rate of diffusion: substances which increase the former reduce the latter. The experimental difficulties are very considerable and are explained in the literature. Among more recent papers on the subject are those by O. v. Fürth and F. Bubanovic,¹⁰ and by W. Stiles.¹¹

The fact that both the swelling and the drying of gels are controlled by diffusion involves some consequences which, considering that they may have an important bearing on histology and related subjects, have not yet received adequate attention. If a body of gel is bounded by a surface in which the radius of curvature changes very quickly or (as in polyhedra, cylinders bounded by plane ends, &c.) discontinuously, diffusion to or from regions adjacent to tracts of surface with low or zero-radius takes place more rapidly than from the rest. The result is that a body of gel does not remain similar to itself during swelling or drying, but undergoes successive deformations which may be considerable. The effect is particularly marked in drying; thus, cylinders with plane ends at first dry more rapidly round the circular edges, which contract, the profile becoming that of a barrel with convex ends. As the material forming the edges becomes less permeable, the large surfaces dry more quickly, and the final shape is, approximately, a single-shell hyperboloid with concave ends. On allowing such a body of dry gel to swell again, the original shape is not necessarily restored; the reason for this alteration in the capacity of absorbing water is obscure.¹²

The foregoing summary—though necessarily restricted by considerations of space—may give the reader unfamiliar with the literature some idea of our present knowledge. The two great problems to be solved must now be set forth briefly. They are (1) the elucidation of the structure of elastic gels, and (2) the explanation of the phenomenon of swelling. As regards the former, there is at present a fundamental divergence of opinion, inasmuch as some authors (H. Procter, W. Pauli, and J. R. Katz) maintain that elastic gels are *homogeneous* systems, *i.e.*, solid or (H. Procter) “semi-solid” solutions. The evidence for this view is set forth at length in a very exhaustive monograph by Katz.¹³ The other school (W. B. Hardy, Wi. Ostwald, Wo. Ostwald, S. C. Bradford, Dorothy J. Lloyd) consider gels to be heterogeneous systems, but differ regarding the state of aggregation of the phases. Ostwald, in particular, considers gels to be *systems of two liquid phases* having an interfacial tension, while some of the other investigators incline to the view that the properties of gels are best accounted for by assuming some sort of network or cellular arrangement of *solid* phase permeated by liquid. Speaking generally, these rival theories are based on the consideration of a limited number of selected properties, and a great deal of further work is required, probably on quite novel lines, before a definite conclusion commanding universal acceptance can be reached. The author feels, in particular, that the elastic properties have received insufficient attention, and

has attempted, as a first step, to examine whether they are compatible with the assumption of two liquid phases possessing interfacial tension,¹⁴ the result being negative if the assumptions necessary to allow of mathematical treatment are granted.

As regards the phenomenon of swelling, we have at present no explanation whatever why certain substances swell in a comparatively limited number of liquids. In the case of proteins, which have received the greatest attention, conditions are enormously complicated through salt formation and electrolytic and hydrolytic dissociation, and here, as in other problems of colloid chemistry, substantial progress is to be expected only from the study of non-aqueous systems, of which a large number is certainly available. This is also the view expressed by Katz in the monograph already quoted: "Swelling in organic solvents would, perhaps, be more important for an investigation in the service of pure physical chemistry than swelling in water." It is greatly to be hoped that the present discussion may induce competent workers to examine this—equally neglected and promising—field.

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THE STRUCTURE OF ELASTIC JELLIES

BY

PROFESSOR H. R. PROCTER, D.Sc.

When I was invited to take part in this discussion, I expressed the desire not to be entrusted with the responsibilities of an introducer, but to leave this in younger and more vigorous hands. As, however, I have been put down for the part, I will endeavour to fulfil it as best I may, and appeal for indulgence in any inevitable shortcomings.

I take it that the three possible views of such a structure are—

1. That of a simple emulsion of spherical or more or less distorted globules in a liquid medium.

2. A sponge-like structure, containing in its pores either the suspension liquid, or a liquid solution of the colloid, but two-phased in the sense that the pores are of microscopic and not molecular dimensions, and open ended, and that the two phases are therefore chemically independent and mechanically separable.

3. A more or less solid solution of the exterior solution in the colloid, in which both constituents are within the range of the molecular attractions of the mass, and which are in chemical and electric equilibrium with the external liquid when one exists. Such a solid solution therefore constitutes a single phase in equilibrium with a real or virtual external solution.

I take it that the first of these conceptions so little explains observed facts that it is now no longer maintained, and that I may devote my time to the consideration of the two remaining, which mainly differ on the question of size, since both postulate or admit a network framework. The difference, however, is not unimportant, since microscopic size excludes or complicates the simple chemical causes which are sufficient for the solid-solution view, and involves mechanical structure which itself demands explanation. Of course the molecular view does not preclude the possibility of there being microscopic pores, closed or open to the surface, but it does not assume that they take part in the equilibrium. Such interstices can undoubtedly be produced under certain conditions.

Let me now make clear my conception of the chemical or molecular theory, which demands no assumption but that of the chemical and physical laws which are everywhere accepted.

For the sake of simplicity I will confine myself to gelatine as the elastic colloid, and to solutions of hydrochloric acid on the acid side of the isoelectric point, and so dilute that without sensible error we may assume them as fully ionised, or at least of equal ionisation to the gelatine chloride. Gelatine under these conditions acts as a weak base, and combines with acid to form an ionisable salt, but as the base is a very weak one the salt is freely hydrolysed, and can only exist in presence of excess of free acid. The jelly-mass will therefore consist of gelatine chloride, free acid, and neutral gelatine, in proportions which are determined by Wilhelm Ostwald's well-known hydrolysis equation, and the concentration of the external acid solution. There is every reason to assume that neither the neutral gelatine nor the

gelatine ion exert any sensible osmotic pressure, though, if they do so, it will only somewhat increase the swelling of the jelly. Now the external acid contains H^+ and Cl' ions in equal numbers, while the jelly contains not only the equal numbers of H^+ and Cl' ions of its free acid, but the Cl' ions of the ionised gelatine chloride, and therefore Cl' ions in considerable excess of the H^+ . Now osmotic equilibrium demands that the sum of the diffusible ions in the liquid and the external solution should be equal, while the thermodynamic equilibrium used by Donnan requires that the products of $H^+ \times Cl'$ must also be equal in both, and as the sum of two unequal numbers is always greater than that of two equals giving the same product, it is impossible with finite quantities to fulfil both equations simultaneously, and there must always be a small excess of osmotic pressure in the jelly, which causes it to swell. Of course under these conditions the jelly would tend to swell to infinity and ultimately dissolve; and since it does not do so, we must assume some opposing force, and the only possible one appears to be the elastic cohesion of the jelly, which implies some sort of connected structure. This force obeys Hooke's general law of elasticity, that "the stress is equal to the strain," and in this case increases in proportion to the volume of swelling, and it may therefore also be stated that the energy opposing swelling is equal to the surface-energy created by a real or virtual extension of the surface proportional to the increase of volume. By this is not meant that an actual extension of surface actually occurs, but that the attractive forces of the molecules which constitute the "internal pressure," have been overcome to a similar extent. This generalisation which, if true, applies to all cases of volume-elasticity of a like kind, has an interesting corollary. Surface-tension, as shown by Stefan's law, has a simple relation to the heat of volatilisation, and therefore elasticity must have a similar relation. This should also imply a relation between the elasticity of a jelly and its heat of melting.

I have purposely avoided all mathematics in what I have said, but the fact remains that all the phenomena of gelatine swelling are connected by quite simple equations derived from its chemical equivalent weight and ionisation-constants only, and that curves plotted from these equations agree within experimental error with experimental results. Such concordance cannot be fortuitous, and is not shown by any other theory yet proposed.

As to the nature of the network I postulate nothing, but it must be a very open one, since diffusion takes place through it with almost the same speed as through still water, and considering the chain-character of proteids, it seems not unlikely that the act of "setting" consists in the formation of tenuous and possibly flexible crystals, which interlace and possibly anastomise. Melting them would consist in the breaking up of this complex into smaller and smaller fragments, with increased dispersity and lessened viscosity with rising temperature, and over $70^\circ C.$, the solution becomes probably nearly molecular. The slow increase of viscosity with time at lower temperatures would depend on the comparative slowness of crystallisation.

It is now in place to point out a few of the difficulties of the sponge-structure theory. Firstly, if the liquid phase is contained in open pores, its ionisation cannot produce an internal osmotic pressure, since there is no semipermeable surface, and nothing to prevent its diffusing into the outer liquid. Also Donnan's membrane-potential theory is inapplicable for the same reason, and because it depends

on electrical attractions and repulsions which are only operative at molecular distances, and is an equilibrium between two phases only, and not, as in the sponge structure, between three. Though it has hitherto proved impossible to make a direct measurement of the Donnan potential, it is easily calculated when the ionic concentrations are known, and in the case of gelatine and acid only amounts to a few millivolts, and it can be shown experimentally that when it is opposed to an E.M.F. of the same value no current is produced and the combined E.M.F. is zero.

Miss D. J. Lloyd's view that the solid phase of the sponge-structure is composed of isoelectric gelatine also presents difficulties, since the firmness and contraction of the jelly increases with addition of acid beyond the point of maximum swelling, and in N/10 acid is a firm and consistent jelly, while it is shown by the combination curve that at this point the conversion into gelatine-salt is almost complete.

The phase law, if it is applicable to these equilibria, also tells against the two-phased structure, which with a liquid phase forms three phases, with three constituents, gelatine, water and acid (or base), and therefore only two "degrees of freedom," while it is known that temperature and the concentrations of acid and water are all variables. It may be here noted that the phase-law also gives a possible explanation of the Paul von Schroeder effect if it really exists. By bringing the jelly from complete immersion in water into its saturated vapour, a third phase is introduced, and one of the freedoms disappears, so that it is quite possible that equilibrium with the vapour can only exist at one particular degree of swelling.

Perhaps in conclusion I may mention one or two cases in connection with the structure of jellies in which I think experimental results have been misunderstood, or misinterpreted. The first of these is the fact that water, or a weak proteid solution, can be squeezed out of jelly by mechanical pressure, a fact which I observed accidentally some 30 years since in a technical experiment on the filter-pressing of gelatine solutions, and which has been held to prove the two-phased character of the jellies, but which, of course, might have been foreseen as a necessary consequence of ordinary osmotic laws. A jelly behaves exactly like an osmotic liquid confined in a semi-permeable membrane, say like dilute alcohol contained in a bladder. Placed in water this will swell till the osmotic pressure of the alcohol is balanced by the elastic tension of the bladder, but if to this a mechanical pressure be added, a corresponding portion of the water will be expelled, possibly with a little alcohol also, as the semi-permeability of the bladder is not quite perfect. In the same way water is expressed from the jelly, and as commercial gelatine always contains some soluble products of its hydrolysis, some portion of these will be expelled with it.

Another mistaken conclusion is that the progressive combination with acids as the latter are concentrated proves the existence of a large number of combining basicities, which gradually come into action. Such a gradual formation of the gelatine-salt is a necessary consequence of the ordinary hydrolysis law, and if such additional basicities really existed it would be very strange if they did not produce kinks in the regular hydrolysis curve which do not seem to exist. It was to account for such an apparent deviation that I adopted the idea of a second valency, but it was much more probably accounted for by the slight hydrolysis of the gelatine molecule which appears to take place with increasing concentration of acid. There can, I think, be no doubt that the actual combining equivalent is in the

neighbourhood of 800, though the molecular weight may be much greater, and it is quite possible that this is an average of several proteids containing different amino-acids, but otherwise similar in structure. The number given represents of course only the smallest chemical combining quantity, and it is probable, especially at low temperatures, that the actual molecular weight may be much greater through polymerisation. Paal found a molecular weight of only about 900 by boiling point determinations.

The fact just mentioned of the impurity of commercial gelatine as a single proteid of course renders such attempts as Miss Lloyd's to calculate the molecular weight from the amino-acids found for the present abortive. We are engaged at my laboratory in the attempt to purify gelatine further by separation at its isoelectric point, and perhaps by subsequent fractional precipitation, and if we succeed, shall repeat, van Slyke's determinations.

Leeds, 19 October 1920.

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THE REVERSIBLE SOL-GEL TRANSFORMATION

BY

S. C. BRADFORD, B.Sc.

The numerous theories of gel structure fall naturally under three heads. The first class of one-phase, or molecular systems, resembles the "super-cooled liquid" theory of glass, and has difficulty in explaining the loss of mobility which occurs on cooling. The second, or two-phase liquid-liquid, type suffers from the defect that no emulsions are known which have really the properties of gels. Moreover, mathematical analysis shows¹ that this structure does not readily account for the elastic properties of gels. The third, or two-phase solid-liquid, type is the oldest and most natural. It suggests immediately that the almost infinite increase in viscosity which takes place, with slight change of temperature, during gelation is due to the gradual separation of solid from solution and appears to give² a simple explanation of all the properties of gels.

In order to understand fully the reversible sol-gel transformation from this point of view, it seems necessary to know the true relation of sols to ordinary solutions. A gradual transition in properties from coarse suspensions through sols to true solutions is generally assumed. This does not readily suggest an explanation of the marked differences in behaviour to electrolytes which occur. It seems probable, however, that sols are related more closely to metastable solutions, the behaviour of supersaturated solutions to electrolytes does not appear to have been studied up to the present. Recent experiments on banded precipitates in gels appear to indicate that supersaturated solutions may be sensitive to electrolytes like sols.

Bechhold³ had previously mixed solutions of silver nitrate and ammonium chromate in the presence of varying amounts of ammonium nitrate and found that, with increasing ammonium nitrate the precipitate of silver chromate gradually decreased, disappeared, and then gradually increased again. A similar effect was found with potassium sulphate instead of ammonium nitrate. The experiments indicate both a change in the actual solubility of silver chromate and in the metastable limit, since concentrations could be found at which a precipitate was produced only after standing. With citric acid, as a trivalent anion, there was an enormous increase in the value of the ionic product at which precipitation of silver chromate occurred, which varied with the amount of citric acid. When the metastable limit was reached a large excess of chromate was deposited. Experiments in gels indicated a similar effect in the case of potassium citrate and soluble phosphates. The effect may be like that of the hydrogen ion, which tends to prevent the precipitation of positive sols, or of the aluminium ion, which changes the sign and increases the stability of gold sols. The experiments are being continued. So far they afford evidence of considerable sensitiveness to electrolytes on the part of ordinary supersaturated solutions.

If this be so, suspensoid sols would correspond more closely to metastable solutions and emulsoid sols to true solutions. Indeed the characteristic properties of colloid solutions may be due to one

or both of two separate causes: supersaturation and particle size. From this point of view there should be substances which exhibit colloid properties merely on account of the large size of their molecules, or, of a chemical, or other, tendency to aggregation. Their sols would be comparatively little affected by electrolytes and might be treated as an extreme case of ordinary solutions.

Glutin and δ -galactan appear to fall in this class. The molecular weight of gelatine has recently been estimated¹³ at about 10,000, which would give a molecular diameter of 1.75μ . Its rate of diffusion is very low and, consequently, its velocity of crystallisation or separation from solution. From von Weimarn's formula such bodies should form sols on heating and gels on cooling.

For, if such a substance of very low diffusivity be treated with a liquid in which it is only slightly soluble, the Nernst-Noyes formula

for the velocity of solution, $V = \frac{D}{\delta} S (L - c)$, shows that, on heating,

solution would take place slowly and the sol stage persist. The velocity of crystallisation, on cooling, would also be very small, so that a large excess concentration would be generated, and, if v .

Weimarn's formula, $N = K \frac{P}{L}$, applies, P would become great, L small and K a maximum, so that N would be very great and a gel would be formed.

As has been shown,⁴ the formula is open to criticism as being merely empirical and the meaning of certain terms somewhat indefinite. And it has been suggested that the equation might preferably be written

$$N = U \cdot \frac{P}{L}$$

where U is a function, to be determined, of the viscosity of the reaction medium and of the size and structure of the particles in solution, whether due to physical aggregation or to chemical complexity. The experimental evidence shows that, as N increases, the precipitate passes through stages in which it appears as (1) large complete crystals only after some years, (2) ordinary crystals in a short time, (3) growth figures or needles, (4) amorphous, frequently showing spherical grains, or spherites, under the microscope, and (5) as a gel which cannot be differentiated by present-day optical instruments. The formula, therefore, offers a reason for the occurrence in the colloid form of such substances as those considered above.

By inoculation of supersaturated solutions, von Weimarn has demonstrated that in every stage, except the two extremes, the solid phase is crystalline; from which he infers that it is also crystalline in sols and gels. Debye & Scherrer's⁵ X-ray analysis confirms this in a number of cases. The special case of gelatine will be discussed below.

Almost all the phenomena of gelation indicate a connection with the process of crystallisation. The properties of supersaturated solutions have frequently been observed in the case of both suspensoids and emulsoids. Gold separates spontaneously from sols of more than a certain concentration, and the precipitation is hastened by the addition of a few drops of a second solution of colloid gold. Gelatine gels more quickly if solid gelatine be added. Rubber emulsions behave in the same way. The variation of the gelation temperature with concentration⁶ strongly suggests crystallisation. And this is supported by the temperature increase in the concentration of solid remaining dissolved in the mother liquor expressed from gels.⁷ The crystall-

isation theory removes the difficulty of explaining the viscosity changes in emulsoid sols in accordance with Einstein's formula, since the changes are due to variation in the number of particles as well as their size. The osmotic pressure changes must be due to the same cause.

Moreover, there are numerous organic substances known which behave exactly as indicated by von Weimarn's formula, and can be obtained as desired in the ordinary crystalline, or in the gel, form. The sodium salt of acrylic acid crystallises from dilute solution as lenticular needles, while the boiling saturated solution sets to a "structureless" jelly. This seems to be due to a chemical tendency to aggregation. Examples could be multiplied indefinitely.

Except, therefore, that they are not readily obtained in the crystalline form, there seems to be no reason for supposing that gelatine and agar are exceptions to the rule. Gelating 2 per cent. gelatine⁸ shows gradual development of submicrons from four or five, showing Brownian movement, in a square division of the field, with a side of 9μ , to 80 to 100 at rest in the same area. If the liquid be expressed from the gel, the submicrons are also visible ultramicroscopically¹⁰. In the case of reversible gels of 5-dimethylaminoanilo-3:4-diphenylcyclopentene-1:2-dione,¹⁰ the ultimate particles were visible as microscopic spherites of 10μ diameter.

It is therefore to be expected that, by suitable modification of von Weimarn's factors, as, for instance, by reduction in the value of P, it should be possible to obtain the ultimate particles of gelatine of a microscopic size. Although the experiments are still in a preliminary stage the results strongly confirm the theory. In the first experiments, already described,¹¹ 0.3 and 0.5 per cent. gelatine, sols were allowed to evaporate spontaneously at room temperature. They were only slightly opalescent at first, but developed, within a few days, an extraordinarily dense opalescence with the eventual deposition of a slight buff-coloured precipitate which was seen to consist of spherites up to about 2.8μ in diameter. Except for the presence of bacteria, the appearance was much the same whether or not 0.1 per cent. mercuric chloride was present as antiseptic. Since the opalescence first appeared within a few hours, decomposition of the gelatine is unlikely. And it was found that warm 4 per cent. gelatine sols do not give a precipitate on standing with saturated mercuric chloride solution. The precipitate must therefore be due to gelatine which has been obtained of microscopic size in accordance with theory.

Experiments under aseptic conditions gave comparable results. Warm 0.4 per cent. gelatine sols were filtered into clean test-tubes, the liquid boiled and the ends of the tubes immediately drawn out and sealed. These similarly, though more slowly, developed an opalescence. In three weeks it had become almost opaque and at the same time the opalescence was observed to be settling down in the tube (Fig. 1). Assuming a density of 1.16 for the falling particles, the rate of fall, 14.9 mm. in 37 days, corresponded to a diameter of about 0.1μ . The microscopical appearance, six weeks later, was that of innumerable grains just too small to be distinguished separately. But a fair number of larger grains were present up to about 0.6μ . In another experiment 0.4 per cent. gelatine, in small test-tubes, was allowed to evaporate at room temperature over concentrated sulphuric acid contained in larger tubes, which were sterilised and sealed. The liquid became turbid and half gelatinous, and had a similar microscopic appearance to that in the previous experiment, though with fewer larger particles.

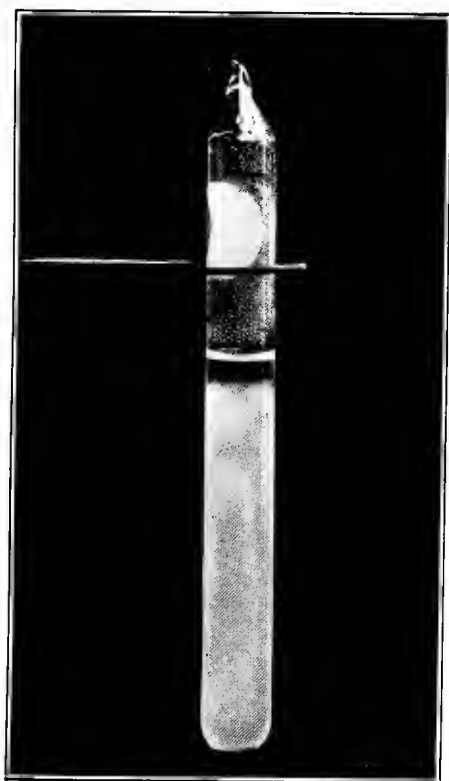


FIG. 1.

N may also be decreased by increasing L by working at higher temperatures. Spontaneous evaporation of 5 per cent. gelatine sols at 31° for 78 hours produced a smoky-looking jelly, which was still viscous in parts, but set on cooling to a stiff mass. The microscope showed this to be full of grains, which were just visible even with a 1-inch objective. Working at 40° gave similar results. With a magnification of 200 the grains appeared perfectly spherical up to about 1μ in diameter. Many of these were aggregated into clusters somewhat like bunches of grapes. With crossed nicols a glowing point could be made out in the centres of some of the grains. In these experiments camphor was used as antiseptic.

There is, therefore, good reason for regarding the reversible sol-gel transformation as an extreme case of crystallisation, due to the very small diffusivity, and consequent minimum velocity of crystallisation, of the gel substance. With falling solubility on cooling, this necessitates the accumulation of an enormous excess concentration, with great increase of viscosity, and gives a maximum value of N in von Weimarn's formula corresponding to the gel state.

It has already been shown² that this view is compatible with all the known properties of gels, as well as indicating new facts. The ultimate crystalline particles of different gels may differ in form according to the nature of the gel substance. The actual structure in a given case is difficult to determine. There are, however, certain phenomena which give some indication of the form of the gelatine particles. It has been shown² that complicated organic substances tend to crystallise in the form of spherites. Regarded as an extreme case of twinning, this is obviously the form in which a body can most quickly be deposited. Von Weimarn's experiments show that, as the dispersity of the precipitate increases, the last stage in which the individual grains can be recognised is frequently that of spherical particles. In the experiments described above gelatin always appears in the spherical form. It seems likely that in the gel state the particles of gelatine are also of the same form. This agrees with the gradual increase in the number of discrete particles viewed ultramicroscopically in the gelating sol, and with the ultramicroscopic appearance of the resulting gel. It is further supported by the lenticular shape of gas bubbles in the gel.¹²

Since spherites consist of a great many radiating filaments, if it be assumed that the deposition of solid gelatine occurs when the particles have reached a certain size, it would be expected that, when this limiting size should be reached, the filaments would hardly have attained a cross-section greater than one or two molecules. Such a structure would not give two adjacent planes, in the space lattice of the gelatine molecules, which could give interference of mono-chromatic X-rays, which agrees with Scherrer's results. Or, it is possible that the lack of interference might be due to the great size of the gelatine molecule.

The above considerations suggest a structure for gelatine gels comparable to that of a pile of shot, but, as previously pointed out,² they leave open the question as to whether the spherites are themselves united into a framework. The problem is complicated by the fact that the skins of gelatine gels show elastic properties greater than those exhibited by the internal jelly. The formation of the skin is probably due to further precipitation at the surface, due to adsorption and evaporation, so that the gel particles become felted and cemented together. It seems unlikely, therefore, that a gel which had been dried throughout,

as in the case of ordinary sheet gelatine, would return to its original state by soaking in water. Consequently it is desirable to use freshly prepared gels in experimental work. Almost all the experimental results quoted in favour of a network within the gel could be explained by the presence of the skin, as, for instance, the gradual squeezing out of liquid from a swollen gel.¹³ Moreover certain facts appear to indicate that the particles in the interior of the gel are not always united, or are at least easily separated. The lenticular shape of gas bubbles has already been quoted. A gelatine cylinder, hung up by one end in a moist atmosphere, tends to become pear-shaped. Gelatine gels contract in the direction of greatest length when moderately heated, owing to the expansion of the gel within its skin.² A gelatine cylinder diminishes in breaking stress on cutting the skin. Three cylinders of 5 per cent. gelatine 24 hours old showed breaking stresses (gram)/(cm²) of respectively 16.9, 25 and 25 for the interior gel, and 33, 66 and 133 for the skin, giving a ratio varying from 2.1 to 5.3. On the other hand, aggregation must be assumed in the case of the skin, and insufficient concentration is the only reason why the particles should not grow together within the gel. Crystallisation experiments show a marked tendency of the spherulites to aggregation. The remarkable behaviour of the 0.4 per cent. gelatine sols sealed in test-tubes somewhat supports this view. The tubes were not kept in a thermostat and showed a gradual increase in rate of falling of the particles, which may have been due to increase in size. After about 40 days the room temperature was lower and the rate of fall of the particles had diminished considerably. A little later it was observed that the cloudiness below the clear liquid, appeared to have set to a gel, which seemed to be just coherent, but broke up on inverting the tube.

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NOTE added 29th October, 1920.

The undisturbed gel resulting from the setting of the 0.4 per cent. gelatine solution, described above, was observed to contract beneath the clear liquid. The surface of the gel began to shrink away from the side of the tube, and, in seven days after setting, the whole of one side of the gel had come away from the tube, leaving a clear space of about 1 mm. At the time of writing, the shrinkage was still going on. Since no attempt had been made to adjust the gelatine to the iso-electric point, the shrinkage is of interest in connection with a similar contraction currently described (D. J. Lloyd, *Biochem. J.*, 1920, **14**, 584) of a 1 per cent. gel prepared from iso-electric gelatine.

THE STRUCTURE OF GELS

BY

J. O. WAKELIN BARRATT, M.D., D.Sc. (LOND.),
BEIT MEMORIAL RESEARCH FELLOW

The current view of the constitution of gels is that of fluid droplets of extremely minute dimensions enclosed in a solid framework comparable, in a rough and ready way, to a honeycomb. The idea of this type seems to have had its origin in a suggestion of similarity of gel structure with that of the stems of young plants, which though containing, perhaps, as much as 90 per cent. of water, for the most part enclosed in cells, nevertheless possess considerable rigidity and elasticity.

The earliest attempts to render gel structure visible, which were made with the aid of microscopic methods by Bütschli (1902) and resulted in the display of a foam-like appearance, difficult of interpretation, were unfortunately barren of scientific result. Subsequently the range of microscopic investigation was considerably increased by ultramicroscopic methods, which have now been employed in studying gels by several observers, including Zsigmondy (1912). The result has been to show that gels sometimes are apparently structureless on ultramicroscopic examination, and that when structure is observed this consists, not of liquid droplets enclosed by (solid) septa, as the honeycomb theory requires, but of a mass of intersecting fibrils, which run perfectly straight, and are united at their points of intersection. This fibrillary structure has been studied in gels of soap, barium malonate and fibrin.

The nature of the fibrils and their mode of formation have been the subject of divergent views. Stübel (1914) pointed out their superficial resemblance to linear crystals, and Howell (1916) introduced in this connection the term crystalline gel. Nevertheless, evidence that the fibrils possess the physical characters of crystals is wanting. Barratt (1920), who observed that the fibrils in a fibrin gel are not only remarkably elastic but are also tense, has advanced an hypothesis of their mode of origin from the disperse particles of the sol out of which this gel is formed.

It has been doubted whether gel characters are explicable as the result of fibril formation. This doubt seems to have arisen from the circumstance that, under suitable conditions of experiment, gels in which no fibrillary structure is apparent may be prepared from fibrinogen hydrosol. In my experimental work, however, it has been found that fibrils may be shown to be already formed for a relatively considerable time before becoming visible, being at first amicroscopic and subsequently increasing in size until ultramicroscopic visibility is reached. Moreover, the excessively fine fibrils first seen may, under appropriate experimental conditions, be made to increase in thickness until a diameter exceeding $1\ \mu$ has been reached, this increase occurring at the expense of the continuous phase of the fibrinogen sol. It would appear, therefore, that the real structure of these gels is a fibrillary network, at first amicroscopic and later becoming ultramicroscopic. This type of structure affords

an explanation of the physical characters presented by gels. If the fibrils are excessively fine and extremely numerous, a gel will be formed which, owing to the enormous resistance offered to the passage of water through the interstices of its fibrils, will appear "dry" and rigid, rather than elastic: if the fibrils are coarse and relatively few in number the gel will be moist, fluid will exude on pressure or on spontaneous "retraction of the clot," and a certain amount of elasticity will be observable. The network character of gel structure renders the behaviour of gels in respect of diffusion readily comprehensible. The fibrillary hypothesis of gel structure also affords a very simple explanation of gel filtration: ultramicroscopic and amicroscopic particles and also, under suitable conditions of experiment, large molecules or radicals may be arrested by gel fibrils in just the same way that microscopic particles are stopped by cotton fibres in filtration through filter paper.

REFERENCES

- Barratt, *Bio-Chem. Journ.*, 1920, **14**, 189; Bütschli, *Untersuchungen über mikroskopische Schäume und das Protoplasma*, Leipzig, 1902: Howell, *Amer. Journ. of Physiol.*, 1916, **40**, 526; Stübel, *Pfluger's Archiv*, 1914, **156**, 361; Zsigmondy u. Bachmann, *Kolloid-Zeitschr.*, 1912, **11**, 145.
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The following contribution to this Section of the Discussion was received from **Professor Dr. Zsigmondy** (Göttingen) in response to an invitation :—

The communications by Messrs. Barratt, Hatschek and Bradford* concern problems which have long been occupying me, and which hence particularly interest me. I have been endeavouring to find methods of helping colloid chemistry out of the undesirable condition in which it has been for a long time, a condition of uncertainty which has rendered it possible that two entirely contradictory views could co-exist and be exposed with equal degrees of probability.

The papers quoted repeatedly refer to ultramicroscopic methods. Mention has also been made of another method¹ of studying gel structures of amicroscopic character. This last method is based upon an examination, after van Bemmelen, of the lowering of the vapour tension which liquids undergo in dry gels. John Anderson,² of Glasgow, investigated in this way a gel of silicic acid, and found by careful experiments with several liquids that the gel in question contains hollow spaces of less than 10 $\mu\mu$ diameter. Working by the same method Bachman³ found later that the gelatin jellies, hardened after Bütschli, likewise enclosed much finer hollows than one would expect after Bütschli's microscopic observations. Similar cavities of two different orders of magnitude also occur in cocoa-nut charcoal. This method of investigation deserves further application.

Already before 1914 the various methods of examination of different experimenters had established that the gel structures may vary much more than had been assumed⁴, and that in addition to the apparently grainy structure we meet in the diluted gels of gelatine, agar and silica⁵ very frequently also with the fibril structure to which Barratt draws attention, especially in aqueous soap jellies. It should be pointed out that Barratt's observations of amicroscopic fibrils—which only gradually become visible—can also be made in soap gels.⁶ This observation, and others of similar nature, support the suggestion thrown out by Flade,⁷ that the jellies consist, *in general*, of a texture of (probably) crystalline threads.

This view, however, seems to be contradicted by the ultra-microscopic structure of the diluted gels of gelatine, agar and silica as investigated by Bachmann. In these cases we can observe the formation and agglomeration in flaky groups of freely movable ultramicros (of so far unknown structure). This phase of gel formation must hence not be regarded as a crystalline process, but as an aggregation of already formed ultramicros.

If we were to regard the gel formation quite generally as a crystallisation process, then the assumption of Bradford (development of ultra-microscopic spherites composed of crystalline fibrils) would quite well explain the primary process. Certain facts seem still to be incompatible with this view, however, in the case of gelatine.⁸ Yet it is to be welcomed that this problem is approaching a gradual elucidation; Hatschek, too, comes to a negative result with his argument that the gels consist of two liquids, and this hypothesis hence appears less and less justifiable.

On the other hand I do not quite wish to fall in with the generalisation that the gel formation should always, even in its primary stages, be regarded as a crystallisation process. The colloids display far too much variety to admit of their being brought under one general scheme. We may, for instance, accept the standpoint of Nägeli and assume that the gels (jellies as well as fibrous textures) consist of micellæ (anisotropic ultramicros) and that they break up, when being dissolved, into these constituents, and not into simple molecules.†

I beg here to draw attention to the results of researches which appear not only to support Nägeli's theory, but also, I think, to supply a good basis for the explanation of some other phenomena. The crystalline character of the elements of vegetable fibres had long been doubted in spite of their double refractivity. The crystalline nature of ramie fibre has now been demonstrated by Scherrer with the aid of Röntgen rays. Optically the proof had already been given by H. Ambronn,¹⁰ who has shown, moreover, that the positive double refraction of cellulose turns into a negative refraction on nitration, though the structure of the fibre does not undergo any appreciable change. According to Ambronn this is a case of a pseudomorphosis of nitrocellulose back to the cellulose type. He observed further that the celloidin, obtained by dissolving the nitrocellulose and turning it into a jelly, also shows negative double refraction—when in the stretched condition. With Nägeli and Ambronn I am inclined to assume that nitrocellulose, in being dissolved, does not break up into molecules, or does so at least only to a small degree, the main decomposition being into polymolecular crystalline rods. That view would account not only for the "high molecular weight" of these solutions, but also for the very interesting relation between the viscosity of the solution and the viscosity of its dry residue, which has been pointed out by Sir R. Robertson. We need only assume that nitrocellulose has, in the less viscous solutions, broken up mainly into rod-shaped primary particles, whilst these particles are, in the more viscous solutions, partly united to flaky secondary particles in wide ramifications, to arrive at an explanation of the greater viscosity of the latter solutions and of some other facts. The aggregation of the primary particles to secondary particles would diminish the number of osmotically-effective particles, which would lead to a decrease in the osmotic pressure corresponding to an increase in the apparent molecular weight. The secondary particles enclose ample amounts of the solvent; the volume of the freely-moving particles is hence enlarged, and the viscosity is distinctly raised.¹¹ When the solution is dried, the irregularly grouped particles will not all come to lie parallel to one another. As a consequence the dry film will enclose ultramicroscopic cavities, and its strength will be diminished.

By offering this presumably useful suggestion I should not like to give rise to the impression that I consider all the riddles of the colloid chemistry of nitrocellulose to be solved in this way. I think, however, that Nägeli's hypothesis, though not always relevant, yet enables us to arrive at a clearer understanding of some colloidal phenomena.

* Dr. Zsigmondy had not seen the papers by McBain and Willows and others when sending in his contribution.—ED.

† The jelly formation would then be based upon an aggregation, devoid of order, of the structural elements considered to have previously been freely movable and of rod shape.

¹ Zsigmondy, *Kolloidchemie*, 1st edition, chapter 60 (1912); 3rd edition, chapters 62 to 62 (c), 1920; also Zsigmondy, Bachmann and Stevenson, *Zschr. anorgan. Chem.*, **75**, pp. 189-197 (1912).

² J. Anderson, *Inaugural Dissertation*, Göttingen, 1914, and *Zschr. phys. Chem.*, **88**, pp. 191-228 (1914).

³ W. Bachmann, *Zschr. Anorgan. Chem.*, **100**, pp. 1-76 (1917).

⁴ Compare the summary, *Physikal. Zschr.*, **14**, pp. 1098-1105 (1913).

⁵ Alcoholic sodium palmitate jelly also solidifies to a gel showing similar ultramicroscopic discontinuities, *Koll. Zschr.*, **11**, p. 154 (1912).

⁶ Zsigmondy and Bachmann, *ibid.*, **11**, p. 150 (1912).

⁷ Flade, *Zschr. anorgan. Chem.*, **82**, pp. 173-191 (1913).

⁸ Scherrer concludes from his Röntgen ray examination that gelatin consists of two amorphous substances; *cp.* Scherrer's contribution to Zsigmondy's *Kolloidchemie* (3rd edition, 1920).

⁹ *Ibid.*, p. 408; *cp.* also the photogram, Table VII., bringing the crystalline structure out very well; the individual parts seen are probably very thin amicroscopical parallel fibrils or rod-shaped crystals.

¹⁰ H. Ambrohn, *Zschr. f. Wissensch. Mikroskopie*, **32**, p. 43 (1918); *Kolloid. Zschr.*, **18**, pp. 80 and 273 (1916), and **20**, p. 173 (1917); Summary in *Göttinger Nachrichten*, 1919, No. 2, pp. 299-320; Brief Summary, Zsigmondy, *Kolloidchemie*, 3rd edition, p. 112 (1920).

¹¹ *Cp.* Zsigmondy, *Kolloidchemie*, chapter 27, and v. Smoluchowski, *Kolloid. Zschr.*, **18**, p. 190 (1916). By "freely-movable" particles are here understood both the primary particles and the secondary particles, together with their enclosed liquid.

DISCUSSION

Prof. J. W. McBain and Miss E. Laing : Soap solutions are probably the simplest examples of gelatinising colloids. They present unique opportunities for precise investigation, because all of their properties are reproducible at will and there is no uncertainty with regard to the constitution or molecular weight of the molecules concerned. It is for this reason that perhaps I may be permitted to refer to some experiments carried out by Miss Laing in the Bristol laboratory which appear to be of general significance for the theory of gels. The following remarks are taken from the summary of a paper which we have recently submitted for publication to the London Chemical Society.

1. We have discovered that a soap solution of one and the same concentration and at any definite temperature may be prepared in three characteristic states; namely, clear fluid sol, transparent elastic gel, and white opaque curd. The latter have often, but erroneously, been called gels.

2. The sol and gel forms of a solution of sodium oleate are identical in osmotic activity, concentration of sodium ions, conductivity and refractive index; this proves that identical chemical equilibria and constituents are present in the two cases. The sol and gel differ only through the mechanical rigidity and elasticity of the gel form.

3. The quantitative identity of conductivity in sol and gel is irreconcilable with all theories of gel structure hitherto advanced, with the exception of the micellar theory of Nageli of 1858, which was resuscitated by Zsigmondy and Bachmann in 1912, and which is strongly supported by many lines of evidence referred to in the present paper. The colloidal particles in sol and gel are the same; but whereas in the former they are independent, in a fully-formed gel they become linked up, probably to form a filamentous structure. It is probably the particles of neutral soap, and not the ionic micelle, that exhibit this behaviour.

4. The formation of soap curd, in clear contradistinction to gelatinisation, is analogous to a process of crystallisation, neutral soap separating from the solution in the form of curd fibres of microscopic or ultramicroscopic diameter. This is shown by the drop in conductivity and osmotic activity and confirmed by direct and indirect analysis in addition to observations with the ultramicroscope. Coagulation is thus sharply distinguished from gelatinisation.

These results are of general applicability on account of the detailed similarity of the properties and behaviour of soaps with that of the gelatine salts and of the silicates.

The paper referred to contains a detailed discussion of the very numerous lines of evidence which support this filamentous, fibrillary or streptococcic structure of gels which is indicated by the study of soap solutions.

Prof. A. O. Rankine : There is one piece of work which has not been referred to. It did not receive publication probably because it took the form of a demonstration before the Physical Society about 12 years ago, but it may have some bearing on the subject.

The particular experiments consisted of trying to measure the rate at which the viscosity of a gelatine solution in water increased with time. We made a solution of gelatine and water and cooled it quickly to atmospheric temperature. In these circumstances, it showed at first no solid properties at all, but just behaved like a liquid. The solution was then put into the annular space between two concentric cylinders, the outer one of which was rotated at constant speed. The couple arising from viscosity and acting on the inner cylinder was measured from time to time. The rate of increase of this couple was found to follow an exponential law for some time, but the interesting thing is this: that at a certain point, suddenly—a point which could not be very definitely fixed or predicted—there was a very large increase of the couple. I remember that it was suggested in the discussion by Prof. Lees that this was evidence in favour of setting being due to the formation of linkages between particles which had been previously prevented by the fluid motion from joining up until, at the critical point mentioned, they ultimately succeeded in establishing solidity. That is a piece of experimental evidence, possibly of value, but I have to confess that I abandoned the subject of gelatine because the theoretical side of it seemed to present such insurmountable difficulties.

Dr. E. R. Rideal : There is an interesting piece of work being done in the United States at the present time on silica gel, a gel used in industrial work for the adsorption of gases. Patrick, who has worked out different processes for the preparation of the gel, is of the opinion himself that although a gel can be prepared with only 5 per cent. of water, yet on the adsorption of water, the curves which he has been able to obtain, not only with the adsorption of water, but with the adsorption of gases such as sulphur dioxide, and the vapour pressure measurements obtained therefrom, seem to indicate that the swelling of that gel, at any rate, is due to the process of filling by capillaries with different size pores, and he has made quite a good case for that view-point. On the other hand, according to the work which has been done on thin films, which, of course, was originally started by Hardy and has been continued with great success by Langmuir in America, the first action that takes place is the superficial coating of the silica gel or any other gel with the molecules in an orientated form. One can show that in the case of benzene, for example, that the benzene molecule lies flat down under the surface and consists of six carbon atoms, with three double bonds, so that there is a good deal to be said for the orientation hypothesis within molecular ranges, followed by a general adsorption in capillaries on the subsequent addition of more of the dispersing medium.

Dr. T. Svedberg : As I have already pointed out in my introductory remarks, I think the point of the building up of the network is a very essential one in the theory of gelatinisation, and regarding this I should like to tell you of a very interesting experiment which has been carried out in my laboratory by Dr. G. Börjeson. That refers to a non-aqueous gel of an inorganic substance. It is possible to obtain by electric pulverisation—oscillatory current arc—a sol of metallic cadmium in alcohol with particles only 5μ in radius. If such a solution is allowed to stand in a glass bottle for some time, the particles are oxidized to a certain degree—but only the surface of the particles—and during that time the solution sets to a jelly.

You can turn the bottle over and it is quite solid; but if you introduce a glass rod into the solution and make a few movements in it, the system at once becomes liquid again, and the viscosity is scarcely greater than that of pure alcohol.

Mr. E. Hatschek : What is the concentration of the cadmium gel?

Dr. Svedberg : The minimum concentration seems to be about 0.2 per cent., but the phenomenon is more marked at somewhat higher concentrations, e.g., 0.5 per cent.

Mr. S. C. Bradford (*communicated*) :

The persistence of the optical strain in a gelatin gel after the removal of the mechanical stress, recorded by Mr. Hatschek, is most curious. This is the more difficult to account for in the absence of a satisfactory explanation of the ultimate cause of the optical appearance. It may safely be assumed, however, that the optical effect is due to the mechanical strain. In this case the crystallisation theory of gelation appears to offer a possible explanation of the phenomenon.

Gelatine and a few other well-known gels are remarkable for their stability. Most substances, which can be obtained in the gel form under suitable conditions, rapidly develop macroscopic crystals. On the crystallisation theory, the permanence of the natural gels is explained by the insolubility, and particularly the very low rate of diffusion, of the gel substances. With lapse of time, however, visible crystals should develop. Evidences of slow crystallisation in silicic acid gels have been observed previously. They have now been obtained in the case of gelatin. Some 5 per cent. gelatin gels were sealed in tubes on 3 August. After about 14 weeks the gels have begun to show a distinct opalescence, as in the case of the dilute solutions of gelatin already recorded. The change has not yet proceeded far enough for the separation of water to be noticeable, though there are numerous drops condensed on the higher parts of the tubes.

It seems, therefore, that there is an extremely slow process of crystallisation taking place in gelatine gels by which the larger particles are continually growing at the expense of the smaller ones. The marked increase in the modulus of elasticity during the first 24 hours is probably due to the very slow rate of separation of gelatin from super-saturated solution which requires this time for completion. It may then not be complete. The crystallisation process which goes on subsequently must be much slower than this.

Since gel substance is being deposited on the larger particles in a gel, whether strained or not, in the former case the larger particles will gradually become cemented in their constrained positions, so that, on removal of the stress, the particles will be unable to move, the gel will remain bent, and the internal mechanical strain will continue to account for the persistence of the optical appearance in polarised light. This experiment appears to establish the presence of a framework within the gel.

Dr. J. S. Anderson (*communicated*) :

It may be of some interest to state that Zsigmondy's⁽¹⁾ conception of the structure of the silicic acid gel is supported by the results of an investigation⁽²⁾ which I carried out in Prof. Zsigmondy's laboratory

before the war. According to his theory, the silicic acid gel has an extremely fine porous structure, the dimensions of the pores being amicroscopic. By applying the laws of capillarity to van Bemmelen's results^(*) on the hydration and dehydration of the gel, Zsigmondy estimated the diameter of the pores to be about 5μ , that is, about 200 to 300 times smaller than Bütschli's^(*) estimate of 1 to 1.5μ . In order to test the accuracy of Zsigmondy's deductions, I made measurements of the hydration and dehydration isotherms and of the similar isotherms for alcohol and benzene in the case of a specially-prepared gel. The results obtained seem to indicate the presence in the gel of pores of various dimensions. In applying the laws of capillarity to the calculation of the sizes of the pores the assumption was made, for the purpose of simplifying the mathematical treatment, that these pores are arranged in the form of fine capillaries. The diameters of the largest and smallest capillaries were found to be as follows :—

	Diameter of largest capillaries.	Diameter of smallest capillaries.
Water experiment	5.49μ	2.75μ
Alcohol ,,	5.17 "	2.42 "
Benzene ,,	5.98 "	2.70 "
Mean values -	5.55μ	2.62μ

The agreement between the values obtained in the three experiments is rather remarkable when one considers that the factors, such as density, vapour, pressure and surface tension, which enter into the calculation, differ considerably in the three cases. The results seem to indicate that at least the order of magnitude is correct; this agrees with other properties of the gel, as Zsigmondy⁽⁵⁾ has pointed out. It is difficult at present to state any definite opinion as to the actual form and arrangement of the pores, but it is probable, as the late Prof. Riecke suggested to me, that the orientation of the molecules of the gel substance is such that the total internal surface of the structure forms a minimum area.

A number of interesting data with regard to the probable mean thickness of the walls of the gel structure, the specific gravities of the dry and wet gel, and the velocities of hydration, dehydration,⁽⁶⁾ &c., are also to be found in my paper.

Mr. W. Harrison (*communicated*) :

There is no doubt that many gels possess fibrilar structure, but this does not apply to all gels. Gelatine and cellulose appear to consist of minute portions joined together in a somewhat irregular manner. Photographs of these have been obtained with the cardioid condenser of Zeiss, using sunlight in the middle of June. The objective used was a $\frac{1}{4}$ in., the camera extension being very long. Better results were obtained in this way than with a more powerful objective.

It is probable that the fibrils present in soap gels are crystalline. Liquid crystals are well known, and gelatinous crystals have been observed on many occasions. For example, benzopurpurine and chrysophenine, two dyestuffs used for cotton dyeing, can be obtained in rigid needle crystals. Concentrated aqueous solutions set to jellies which contain long gelatinous needle crystals, some of these so fine

that they can pass almost unbroken through a filter paper with the aid of a vacuum pump.

Cholic acid gives a blue precipitate with iodine, which sometimes forms in clusters of needle crystals which are rigid. Under other conditions, one obtains the same needle-shaped crystals quite gelatinous; they may be bent all shapes by moving the cover glass on the microscope slide. The smallest of these crystals show remarkable vibrations due to impact of water molecules. Among these, one often finds spiral-shaped crystals which twist first one way and then the other, as the water molecules bombard them. The movements of these crystals reminds one of the movement of the spiral bacteria present in the teeth.

It is the opinion of the writer that there are many kinds of structures in gels, just as there are many types of structures in crystals.

The observation of Mr. Hatschek that a gelatine jelly, after deformation by stress, retains its optical anisotropy after the external stress is removed, is apparently a common property of colloids. The writer made similar observations with indiarubber, cotton, wool, silk and other fibres, but found that the anisotropy was due to internal stresses produced by the deformation and disappeared when the substances were treated so as to allow those internal stresses to balance. (Harrison, *Proc. Roy. Soc.*, A, **94**, 460 (1918).)

Referring to the paper by Mr. Bradford, a photograph was taken by the writer (*J. Soc. Dyers and Cols.*, **32**, 32 (1916)), which shows spherical coagulation-forms of starch which might easily be taken as spherites and which may be analogous to the gelatine spherites mentioned by Bradford. It was found that soluble points in a contact surface had a considerable effect in promoting these growths.

In relation to Bradford's recent experiments on periodic precipitation in gels, the writer made a few experiments some years ago, but has had no time to complete them. One interesting result may be mentioned which does not appear to be explained by the various theories put forward up to the present. Using barium ferrocyanide in a gelatine jelly and diffusing into this a copper sulphate solution, periodic rings of brown copper ferrocyanide and of white barium sulphate were obtained, these rings being alternate. With silver sulphate and barium chloride, alternate rings of silver chloride and barium sulphate were formed.

It does not appear that these experiments can be explained by the super-saturation theory, since both these salts are removed from solution by the precipitation. It appears to the writer that, by the use of salt-pairs which are both removed from the reaction medium, one may learn much more about periodic precipitation.

Mr. E. Hatschek (*communicated reply*): Prof. McBain says in regard to soap gels: "The sol and gel differ only through the mechanical rigidity and elasticity of the gel form." This applies to other gels, and it is therefore all the more desirable to explain the origin of this rigidity and elasticity in terms of some internal rearrangement. The micellar theory does not appear to be helpful in that respect. The first difficulty is that McBain's "ionic micelle" is certainly not the same thing as Naegeli's micelle. It accounts for part of the conductivity of the soap solutions, and if the conductivity of the gel is identical with that of the solution, the ionic micelles must move as freely in the former as they do in the latter. Accordingly, Prof. McBain suggests that "it is probably the particles of neutral

soap, and not the ionic micelle, that exhibit this behaviour," i.e., that "become linked up." Whether a micellar structure is postulated for the neutral particles as well does not appear.

As regards the identity of several properties in the sol and gel state, this is not confined to soap. Walpole⁷ has shown that the refractive index of gelatin sols and gels is the same for a given concentration and temperature: indeed, there is no *a priori* reason why there should be any difference. Arrhenius demonstrated, a long time ago⁸, that the conductivity of salt-gelatin water systems was the same in the sol and in the gel condition. As far as osmotic activity—more particularly vapour pressure—goes, there is considerable evidence pointing to their being the same in both states, if they are measurably different from that of the solvent.

As regards "curds," Prof. McBain is, no doubt, right in differentiating them sharply from gels, but the phenomenon is without exact parallel in other typical elastic gels, e.g., gelatine.

The experiment described by Prof. Rankine has often been made with various sols, generally in the capillary viscometer. An exhaustive investigation, e.g., is that by Pauli and Fernau⁹ on ceric hydroxide sol, which forms an irreversible gel on the addition of electrolytes. The results correspond with those obtained by Prof. Rankine: they have given rise to the statement to be found in the literature, that the sol-gel transformation (whether reversible or not) is "continuous." This statement simply means that, as far as the rise in viscosity can be measured, a continuous time-viscosity curve is obtained. A point is, however, reached where measurements are no longer possible, and this is the really interesting region, in which a discontinuity is quite possible and indeed probable.

Patrick's results, quoted by Dr. E. R. Rideal, agree with those obtained by Zsigmondy and his school, referred to by Dr. Anderson. It is, however, only the rigid gel—like that of silicic acid or of tanned gelatin—which, on drying, develops pores that are filled with air and can be filled by imbibition with a liquid other than the original solvent (the latter observation was made already by Brewster on tabashir, a silicic acid gel occurring in the internodal spaces of the bamboo). Drying *elastic* gels do not develop such pores: a dry gel of natural gelatin will not imbibe, say, benzene. The dimensions of the pores given by Dr. Anderson are those of the pores in the *dry* gel, and give no clue to the structure of the fresh gel, nor to that of either a fresh or dry elastic gel.

Prof. Svedberg's example is of great interest as showing the very low concentrations of suitable disperse phase, at which gel formation is possible. In this respect they are not unique: Doehle and Rassow¹⁰ have described the mercury salt of an organic sulpho-acid, which forms gels in concentrations of 0.72 per cent., while camphorylphenylthiosemicarbazide, prepared by Prof. M. O. Forster and investigated by the writer, forms stiff gels in concentration of 0.33 per cent. and "trembling" jellies in concentrations as low as 0.25 per cent.¹¹ Assuming the whole of these concentrations to represent supersaturation, the question arises why similar supersaturations, quite easy to obtain with innumerable other substances, do not lead to gel formation, and what peculiarity of the substance it is on which the phenomenon depends.

Both Mr. Bradford and Mr. Harrison refer to the writer's observations on the survival of optical anisotropy in gelatin gels after the disappearance of the stress. Mr. Bradford's suggestions are quite

consistent with his views, but there is no evidence of the slow change he postulates continuing beyond the first 24 hours or so. It is, of course, quite possible that such changes occur and that no one, so far, has taken the trouble to look for them. Mr. Harrison has found that a similar behaviour is characteristic of other gels, but this would make it all the more desirable to find the explanation of a phenomenon which is certainly, to say the least, unexpected in a system consisting of over 90 per cent. of liquid. The difficulties of the subject are well illustrated by the investigations of Ambrohn on permanently-stretched colloidal strips¹², which were allowed to imbibe liquids of varying refractive index. The accidental birefringence is a function of the deformation and of the refractive indices of both substance and liquid, and may become zero and eventually change its sign when the latter is varied.

Mr. Harrison's suggestions regarding periodic precipitation, viz., the use of salt-pairs which are both removed from the reaction medium, are of great interest and should certainly be followed up.

The writer is also in complete agreement with Mr. Harrison's view that "there are many kinds of structures in gels." There are obvious, and generally acknowledged, differences between the rigid and the elastic gels, to use the current descriptions. There is no evidence that identity of behaviour in either class necessarily implies, still less proves, identity of structure; very eminent authorities like Pauli even consider that many gels are homogeneous systems. Only further research, directed principally to the physical properties, can lead to a solution of this problem.

(¹) R. Zsigmondy, *Z. f. anorg. Chem.*, **71** (1911) 356.

(²) J. S. Anderson, Inaugural-Dissertation, Göttingen, 1914; *Z. f. phys. Chem.*, **88** (1914), 191.

(³) J. M. van Bemmelen, *Z. f. anorg. Chem.*, **13** (1897), 233; **18** (1898), 98.

(⁴) O. Bütschli, "Untersuchungen über die Mikrostruktur künstlicher und natürlicher Kieselsäuregallerten," Heidelberg (1900), 294.

(⁵) R. Zsigmondy, *loc. cit.*

(⁶) For an accurate method of measuring such velocities see J. S. Anderson, *Trans. Faraday Soc.*, **11**, (1915), 69.

⁷ G. S. Walpole, *Koll.-Zeitschr.*, **13**, 241, 1913.

⁸ S. Arrhenius, *Ofvers. d. Stockh. Akad.*, 1885, No. 6, p. 121.

⁹ Pauli and Fernau, *Koll.-Zeitschr.*, **20**, 20, 1917.

¹⁰ Doehle and Rassow, *Koll.-Zeitschr.*, **12**, 71, 1913.

¹¹ E. Hatschek, *Koll.-Zeitschr.*, **11**, 158, 1912.

¹² H. Ambrohn, *Koll.-Zeitschr.*, **18**, 90, 273, 1916.

SECTION III.—GLASS AND PYROSOLS

Discussion on "Glass and Pyrosols" was opened with an Address by **Sir Herbert Jackson, K.B.E., F.R.S.**

The following is a brief abstract of the Address, which the author was unable to prepare for publication :—

The lecturer doubted the relevancy of the subject to a discussion on colloids, although he knew of more than one suspension of colouring matter in glass which was colloidal. It was questionable whether glass was crystalline, but there was evidence of some orientation that approximates to crystalline form in a glass when it is phosphorescent. Almost every glass can be made crystalline or made to separate out crystalline material if kept long enough at a particular temperature. The hydration of the borax or other materials used had much to do with the crystallisation of glass on annealing. The study of the physical and chemical properties of glass from the point of view of composition would no doubt yield valuable evidence as to structure.

The remainder of the address dealt with the constitution and properties of opal and coloured glasses.

Dr. M. W. Travers contributed the following Paper on "The Nature of Glass."

ON THE NATURE OF GLASS

BY

DR. MORRIS W. TRAVERS, F.R.S.

It is commonly stated that glass, in its rigid form, is still a super-cooled liquid, the statement being based upon the assumption that its properties change continuously with change of temperature. As a matter of fact, however, this assumption has been based practically entirely upon qualitative observations. Until quite recently no investigations of the physical properties of glasses had extended over any part of the range of temperature within which glass changes from an elastic solid, through a stage in which it may be described as plastic, to that in which its viscosity has fallen with rise of temperature till the glass is a mobile liquid. In 1917 Twyman (*J. Soc. Glass Tech.*, I., 61) published the results of some experiments carried out with a view to testing the application of Maxwell's equation for the disappearance of stress in a viscous body (*Phil. Mag.*, 1868, **35**, 133) to the problem of annealing glass. He investigated the change in the mobility (rate of change of strain with time under constant stress) with temperature, and found that in the case of all glasses investigated the formula

$$dS/dt = K\varepsilon^{\theta/8}$$

held good, the mobility doubling for every 8° rise of temperature. This must probably be regarded as an approximation holding good over the range of temperature within which the glass may be described as plastic.

A few months ago Tool and Valaseck first called attention to a marked discontinuity in the behaviour of glass in the neighbourhood of the softening point (U.S. Bureau of Standards, *Scientific Papers*, No. 358). They found that above a "critical temperature," T_a , which for all glasses examined, including fused boric acid glass, was about 70° below the softening temperature, the rate of absorption of heat with a rise of temperature underwent a sudden increase, which was maintained up to a temperature T_b , slightly below the softening temperature. The range of temperature T_aT_b coincides with what is called the annealing range of temperature, as determined by the optical method, within which the glass may be regarded as plastic.

Following up this work, Cragoe and Peters (*American Optical Soc. J.*, 1920, **8**, 105) determined the thermal expansion of a number of glasses from 20° to the softening temperature. They again found that all glasses, including boric oxide glass, behaved similarly. The coefficient of expansion remained constant from 20° to very close to T_a . At T_a , which was identical with the critical temperature for the glasses examined by Tool and Valaseck, the coefficient of expansion underwent a sudden change in value, again becoming constant, and remaining so over the greater part of the range T_aT_b , but having a value from four to seven times as great as over the lower range. Above T_b the glass appeared to contract slightly, but it does not appear to be certain that the contraction is real. The fact that fused boric acid behaves similarly to more complex glasses is unimportant, unless it is perfectly

certain that the substance was perfectly pure. Borates, except alkali borates, are very immiscible, and a very small quantity of impurity may be present as a separate phase.

It may be noted that a marked change of volume near the solidifying point was to be looked for as the only way of accounting for the fact that often when two soft glasses of different makes are sealed together they form a perfectly good junction but show a ridge at the point of union. This could not be due to any difference in the rate of contraction over a range outside that at which the glass possessed mobility. Attention may also be called to the fact that if two pieces of glass with optically plane surfaces are placed in contact, and their temperature is raised, there is a definite temperature at which they will become optically united (*Silikat Zeits.*, 1918, III., 213).

These facts point to a very marked discontinuity in the properties of glass in the neighbourhood of the softening point, but they do not furnish any direct evidence in opposition to the idea that glass is a liquid. Within the last week, however, a paper has been published by A. A. Griffiths of the Royal Aircraft establishment (*Phil. Trans.*, A. 221, 163) which throws some light on the subject.

Working with a glass, of which the composition is given in the paper, having a high softening temperature, he found that at temperatures about 730° the load which a fibre could support was determined solely by the surface tension, which decreased linearly with the temperature. Below 730° a fibre was able to support stress, apart from surface tension, this solid stress increasing from zero at 730° to 1.3 lbs. per sq. in. at 657° , and to 24 lbs. per sq. in. at 540° . The magnitude of these effects is still very small over the whole annealing range.

The most obvious alternative to the suggestion that glass is a liquid, is that it is a colloid, and that with change of temperature it passes through the stages,

elastic gel \rightleftharpoons colloidal sol \rightleftharpoons crystalloidal sol.

Looking for some experimental data which would serve as a means of comparing the properties of glass and colloids, I turned to the literature of colloids for information. As Mr. Hatschek has observed in the course of this discussion, no measurements have been made on the thermal and mechanical properties of elastic gels or of the changes which take place in them during gel-sol transformations. Qualitatively there is a distinct resemblance between the changes—

elastic gel \rightleftharpoons sol
and

elastic glass \rightleftharpoons mobile glass.

and I propose to investigate the relationship quantitatively.

The suggestion that glass is a colloid, generally implying some form of a polyphase liquid system, though the meaning of the term liquid applied to the phases which make up each system is rather vague, has frequently been put forward. Barus (*Am. J. of Sci.*, 1898, 6, 270) made use of it to account for the behaviour of glass towards water, and it is indeed difficult to account for apparently erratic behaviour of chemical reagents towards glasses on the supposition that they consist of homogeneous liquid solutions of silica, silicates, &c. (Bibliography, Turner, *J. Soc. Glass Tech.*, I., 1917, 213).

Quincke (*Ann. der Physik*, 1915, IV., 46, 1025) has put forward the suggestion that glass is a jelly-like structure built up of invisible foam walls separating foam cells, the wall and cell contents consisting

of a series of liquid phases each containing several modifications of silicic acid. The observations on which his ideas are based are interesting. In examining the copper aventurine glass, which contain microscopic crystals of copper in a transparent glass, he found that in some cases the crystals developed in lines of similarly orientated octahedra. In other cases groups of crystals appeared to be distributed over curved or plain surfaces. These observations point to the existence of fibrous or cellular structures in the glass. Fibrous structures play an important part in the formation of some gels, such as those of the soaps.

In conclusion I must call attention to the conclusions arrived at by Griffiths (*loc. cit.*) in his paper, which should be read by those interested in this subject. As the results of experiments on the influence of flaws in the tenacity of glass, he finds that this tenacity suffers rapid diminution accompanied by shrinkage, following rapid cooling from the mobile to elastic conditions. Very fine fibres of glass, rapidly chilled, have a tenacity approximating to the theoretical value, which is many times greater than the ordinary experimental value. He concludes that in the mobile state (at $1,400^{\circ}$) the glass consists of molecules arranged "at random." On cooling rapidly the random arrangement momentarily persists, but with lapse of time the molecules arrange themselves first in chains of limited length, and afterwards in surfaces. During slow cooling the chain formation takes place most rapidly over the range $T_b T_a$. The orientation has some relation to the form of the solid produced, accounting for the tendency of glass to flake off from the surface on fracture.

In this connection reference may be made to a well-known phenomenon. If a cut is made round the inner circumference of a glass tube or vessel, as the inner surface is always in tension, owing to the slower rate of cooling, the cut will always extend towards the outside of the tube or vessel, and if it does not do so spontaneously, it will do so on warming the outside. It often happens, however, that when the cut appears to have penetrated to the outside around the whole circumference, a "skin" still remains on the outside which can only be broken by tapping the glass, and even then does not always break through readily or exactly along the line of the cut. At a very small distance from the inner surface the line of fracture bends sharply, becoming parallel with the surface of the glass, so that a thin flake of glass is left projecting from one or other of the several portions. It is frequently stated in chemical literature that the outer layer of a glass article differs from the mass of the glass; but whether it does so in freshly made articles, or only after weathering, is doubtful. The phenomenon referred to above can be observed in any article taken direct from the kiln or lehr, and is probably purely physical in character.

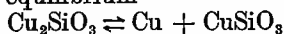
DISCUSSION

Dr. M. W. Travers (*communicated*) :

I fear that the science of glass-making in this, as in other branches, suffers from too much speculation based upon insufficient experimental evidence. Only one series of experimental researches on the coloured glasses, which may be considered to be homogeneous in distinction from the glasses of the gold-ruby type, in which the effect of a range of colouring materials on a range of typical glasses was studied has ever been carried out. I refer to Zsigmondy's work (*Ann. der Physik*, 1901, IV. 4, 60); but of the 90 possible combinations of colouring materials and glasses, he actually examined very few, and only in a few cases did he vary the concentration of the colouring matter in the glass. Other spasmodic investigations have not increased our systematic knowledge of the subject.

I cannot see that any deep mystery attaches to the cobalt and copper glasses which from the results of Zsigmondy (*loc. cit.*) and of Holt and Burgess (*Eng. Ceramic Soc.*, 1905-6, 163), behave similarly to aqueous solution. Cobalt oxide colours boric oxide glass a faint pink, being very insoluble in the glass. The addition of alkali to the boric acid increases the solubility of the cobalt oxide in proportion to the alkali content, and the glass is now blue. Taken with the fact that the boric oxide glass is an electrolyte, and looking at the problem in the light of researches in aqueous solution of cobalt compounds, are we not justified in assuming that the pink and blue colours are due to simple and complex ions? The same remarks apply to green and blue copper glasses; but while the absorption of light by aqueous solution of copper salts has been carefully studied, our knowledge of the glasses is merely qualitative.

The chemistry of the copper ruby glasses has been investigated by Auger (*Compt. Rend*, 1907, 144, 422), who worked on copper aventurine glass, and found that the separation of copper was due to changes in the equilibrium



The separation of copper can, of course, only take place in a glass free from oxidizing agents and dissolved oxygen. Quantitative investigation might show that similar changes took place in the deposition of gold and other elements in a finely-dispersed state in glass.

Sir H. Jackson's statement on water in the batch—its influence on the subsequent devitrification of the glass—must be limited to certain kinds of glass, and detailed information would be of interest. Formerly all flint glass makers used crystallised potash (12 to 18 per cent. water) in their batch, on account of its freedom from sulphates and chlorides, without ill effects.

SECTION IV.—NON-AQUEOUS COLLOIDAL SYSTEMS

Sir Robert Robertson, K.B.E., opened the Evening Session, over which Professor F. G. DONNAN, C.B.E., F.R.S., presided, with discussion on "Non-Aqueous Colloidal Systems with Special Reference to Nitrocellulose."

NITROCELLULOSE

BY

SIR R. ROBERTSON, K.B.E., F.R.S.

INTRODUCTION

The principal applications of nitrocellulose in industry are to celluloid, propellants, artificial silk, collodion and some blasting explosives. In this paper I shall confine myself for the most part to nitrocellulose as used in the manufacture of propellants, and I propose to describe some of the relations that exist between the solutions of cellulose and of nitrocellulose and the gelatinised nitrocellulose after the solvent has been eliminated, together with some work on the characteristics of its solutions.

Most of the modern propellants are colloidal in character, and it is to the nitrocellulose which they contain that this character is to be attributed. As they have no definite crystalline structure, and can be obtained as uniform non-porous masses by the process of incorporation or malaxation during manufacture, they present an unbroken surface to the flame which ignites them, and even under pressure continue to burn regularly from layer to layer. It is this property that has enabled guns to be designed much lighter in weight than for gunpowder, and that has made it possible by suitable choice of thickness of the propellant to secure very high velocities of projectiles (within a narrow margin of a few feet per second from round to round) without undue strain on the gun.

To obtain the degree of regularity in ballistics necessary for accurate shooting it is important for the dimensions of the finished propellant to be within very narrow limits. It has been found that the nature of the nitrocellulose used affects the amount of shrinkage which takes place in the cord after squirting from the die, and it is obvious therefore that the colloidal properties of nitrocellulose gelatinised by means of solvents, either volatile or non-volatile, are of great importance in the study of propellants.

I propose to bring to your attention the results of some work on gelatinised nitrocellulose that has been carried out at the Royal Gunpowder Factory, and the Research Department, Woolwich.

Among the more important aspects that have to be considered are the influence on the product of the nature of the raw material, the influence of the process which it undergoes in being nitrated and stabilised by boiling with water, and the effect of these on the characteristics of the finished material. Among other important properties the viscosity of solutions of cellulose and of nitrocellulose in relation to these aspects clearly required investigation.

TREATMENTS WHICH AFFECT THE VISCOSITY OF CELLULOSE AND NITROCELLULOSE SOLUTIONS

In general, those treatments which would be expected to effect disruption of molecular aggregates (*e.g.*, by grinding or chemical decomposition such as hydrolysis) are found to lower the viscosity both of cellulose and nitrocellulose solutions.

The treatment of the cellulose before solution, with bleaching powder (oxidation) or caustic soda (hydrolysis) in the usual processes of cleaning, reduces the viscosity of its solution in cuprammonium. The viscosity of the solution itself is reduced by exposure to air or light, or even to some extent by simply allowing it to stand for some time. The viscosity of the solution of the corresponding nitrocellulose is found to be affected in the same direction.

With the nitrocellulose, the steam boiling treatments given in the purification process lower its viscosity, but there appears to be a practical limit to the process. When the more easily attacked forms of nitrocellulose have all been destroyed by boiling, the further reduction in viscosity is very slow, and if the cellulose before nitration has been treated so as to reduce its viscosity markedly, no great reduction of viscosity is produced by boiling the nitrocellulose.

In order to produce a nitrocellulose of low viscosity, it is found to be better to reduce the viscosity of the cellulose as far as possible by suitable treatments than to rely on the reduction during boiling of the nitrated product.

It may be mentioned parenthetically on the question of the measurement of the state of molecular aggregation of nitrocellulose in solution, that in a recent paper by Duclaux and Wollman (*Bull. Soc. Chim.*, 1920, **27**, 420), emanating from the Pasteur Institute, while the lower limits of molecular weight of nitrocellulose solutions are shown by measurements of osmotic pressure to be very high, the molecular weight of products of different degrees of viscosity varied from aggregates of 80 times the C_6 formula for cellulose to 270 times in the case of the more viscous samples.

RELATION OF VISCOSITY OF SOLUTION AND OF ITS NATURE TO THE TOUGHNESS OF THE DRIED NITROCELLULOSE COLLOID

In some earlier work the viscosity was measured by means of a viscosimeter of a simple type, and the toughness of the resulting gelatinised dried nitrocellulose in the form of cord was evaluated by determining the least radius of curvature to which the cord could be bent. This method brought out such differences as that a cord of nitrocellulose of 13 per cent. nitrogen content cracked at a radius of curvature of 100 millimetres when acetone had been the solvent, while a cord of nitrocellulose of 12.4 per cent. of nitrogen broke at a radius of 25 mm. again with acetone as the solvent, and at 5 mm. when ether-alcohol had been used to gelatinise it.

From the results of these experiments it was deduced that when the same simple solvent (acetone) was used to gelatinise nitrocelluloses of a high nitrogen content (13 per cent.) the viscosity of the nitrocellulose solution was inversely proportional to the toughness of the resulting cord. The coherence of the dried nitrocellulose was thus found to be adversely affected by the higher state of aggregation of the molecules of the nitrocellulose, as indicated by the viscosity of its solution. This short note on these experiments has been given, as

they illustrate a connection between the viscosity of a solution and the physical consistency of the dried nitrocellulose.

The nature of the volatile solvent also affects the brittleness of the dried gelatinised substance. Thus the dried product made by gelatinising nitrocellulose of 12.4 per cent. nitrogen with ether-alcohol is much tougher than that gelatinised with acetone, and a similar effect is obtained by adding some alcohol to the solvent acetone. Caution has, however, to be observed in this connection, as retention of the solvent in an imperfectly dried substance may give a quite fictitious semblance of toughness to a film of gelatinised nitrocellulose. Thus when films of nitrocellulose of 13 per cent. nitrogen are made with acetone and with amyl acetate respectively, clear acetone films of about 0.5 mm. in thickness (and these can be made by taking precautions to prevent access of water vapour during evaporation of the solvent) seem to be much more brittle than similar films made with amyl acetate. When, however, the latter are dried out so that all the solvent, in this case of considerably higher boiling point than acetone, is eliminated, the film is quite as brittle as that in which acetone is the solvent.

PROCESSES FOR DETERMINING THE VISCOSITY OF CELLULOSE AND OF NITROCELLULOSE SOLUTIONS

It might now be well to refer to some of the methods that have more recently been found most suitable for determining the viscosity of solutions of cellulose and nitrocellulose, and to state briefly the information that study of this property has afforded. Of great importance in this connection has been the application of the falling sphere viscosimeter (*see* Gibson and Jacobs, *J. Chem. Soc.*, 1920, 117, 472) in which the velocity is observed, under standardised conditions, of a steel ball, 0.15 cm. in diameter, falling through the solution, appropriate corrections being made for deviations from Stokes' law on account of the side-effect of the walls and the end-effect of the bottom of the viscosimeter tube. This instrument has had a wide application in the study of solutions of nitrocellulose, and the difficulties inherent in its application to solutions of cellulose in cuprammonium solution, chiefly on account of the need for eliminating air in this estimation, have been overcome (Gibson, Spencer, and McCall, *J. Chem. Soc.*, 1920, 117, 484).

For cellulose dissolved in cuprammonium solution a capillary viscosimeter in which the solution comes into contact only with hydrogen was developed, and the conditions were obtained for the preparation of the cuprammonium solution by a process which gave more reliable results than those described by Ost. By the use of this capillary viscosimeter it is possible to obtain viscosities of more mobile solutions of cellulose in cuprammonium solution than with the falling sphere viscosimeter, for example, below 10 C.G.S. units.

RELATION BETWEEN VISCOSITY OF NITROCELLULOSE SOLUTION AND COHESION OF DRIED NITROCELLULOSE MIXTURES

Reference has been made to a case in which the brittleness of dried gelatinised nitrocellulose was affected by the nature of the original nitrocellulose and associated with high viscosity of the nitrocellulose solution. A similar relationship came to light when a new nitrocellulose-nitroglycerine propellant (R.D.B. Cordite) requiring ether-

alcohol as a solvent was used in quantity during the war, in place of cordite M.D. for which the supply of acetone was insufficient. It was found on pressing the incorporated gelatinised material that the extruded cord exhibited a lack of cohesion and of uniformity in diameter which gave rise to difficulties. An investigation of the nitrocellulose and of the cellulose from which it was made was carried out by the application of the processes mentioned above, and ultimately the cellulose was controlled by the falling sphere viscosimeter. By this means the uniformity of the cellulose was ensured, and a limit imposed on its viscosity. It appeared that the lack of uniformity of the pressed cords of this propellant in this case also was due to an unduly high viscosity of the nitrocellulose, and when measures were taken to control the viscosity of the cellulose itself, no further trouble was experienced.

From a consideration of these two examples, one of gelatinised nitrocellulose and the other of a nitrocellulose-nitroglycerine mixture, it would appear that a high state of aggregation of the molecules of nitrocellulose is not conducive to the toughness that is desirable in a product that has to be handled both during manufacture and after.

The subject of the viscosity of cellulose and of solutions of cellulose was further pursued at the Research Department, Woolwich, by the application of the methods of determining viscosity mentioned above, and some of the results obtained in these investigations may now be considered.

VISCOSITY OF CELLULOSE SOLUTIONS AND THEIR RELATION TO NITROCELLULOSE SOLUTIONS

In the first place, as regards the cellulose itself, the reduction in its viscosity brought about by increase in temperature of the alkaline pressure boiling to which the cotton is subjected, and the influence of increase in the concentration of the caustic alkali in this process in the same direction have been described by Gibson (*l.c.*, p. 481).

Correlations were then made between the viscosity of the cellulose in cuprammonium solution and that of the solution in ether-alcohol of the nitrocellulose made from it, and it was established that although the processes of nitration and stabilising by boiling of the nitrocellulose tended to level down differences, yet there is a general relationship in the sense of higher viscosity of the nitrocellulose made from cellulose of high viscosity, and it was brought out that if the cotton had been incompletely reduced in viscosity by the soda boiling the viscosity of the finally purified nitrocellulose was with greater difficulty brought down by the steaming during stabilisation.

MINIMUM VISCOSITY OF NITROCELLULOSE SOLUTIONS

The viscosity of solutions of nitrocellulose in ether-alcohol was then studied (see Gibson and McCall, *J. Soc. Chem. Ind.*, 1920, 39, 172, T) by the method of the falling sphere viscosimeter, and a suspicion that a small change in the proportion of ether to alcohol affected the viscosity, led to a thorough examination of this variant with ether-alcohol solutions of nitrocellulose of different contents of nitrogen and in different concentrations. It was established that

there was a minimum viscosity at a certain proportion of ether to alcohol, solutions on either side of the minimum being the more viscous, and indeed formed jellies with the higher proportions of either alcohol or ether. The position of this minimum was also found to be independent of concentration, leading to the deduction that this minimum would give the optimum proportions for the solvent used in the process of gelatinisation in the incorporator where the ratio of solvent to substance is necessarily very much less than is any solution of which the viscosity can be measured by the means spoken of above. It may be said that this was verified in practice.

This position of minimum viscosity was found to vary with nitrogen content among those nitrocelluloses which are soluble in ether-alcohol, more ether being required for those with the higher content of nitrogen, and it was also established that the farther the composition of the solution is removed from the point of minimum viscosity, the longer does it take for equilibrium to set in, the process of gelation continuing in some of the mixtures rich in one constituent for a considerable time. It proved to be of importance from a manufacturing point of view to choose the mixture of minimum viscosity, since with the associated proportion of ether to alcohol on the one hand, gelatinisation proceeds with the greatest rapidity, and on the other hand, as this mixture has the maximum fluidity, with the smallest usage of solvent. The practical application of this principle in supply, the large scale experimental work carried out in this connection and the means taken to secure that a nitrocellulose of easy gelatinising properties was obtained by the controlled treatment of the cotton itself are described by Mr. R. A. Punter.

The alcohol used in the above work was of 92 per cent. strength, and it has been found possible by determining the viscosity of a series of binary mixtures of nitrocellulose in ether and alcohol containing varying proportions of water, to obtain a ternary diagram from which the mixture of ether, alcohol, and water that gives the minimum value of viscosity can be read off.

A similar point of minimum viscosity has been found with acetone-water solutions of nitrocelluloses, and it is of interest that the proportion of water in the acetone thus indicated is one which has long been used in the manufacture, having been chosen from other considerations. The phenomena of the gelation of such mixtures are discussed by Masson (*J. Chem. Soc.*, 1920, 117, 819). The relation between viscosity and concentration, as is also the case with ether-alcohol solutions, appears to conform to the Arrhenius logarithmic expression, but only over a limited range.

CONCLUDING REMARKS

The above work has afforded a great deal of information on the nature of the solution of cellulose and of nitrocellulose and forms the basis for theoretical speculation apart from the bearing it has had on manufacture.

The viscosity of the solutions has been proved to have a direct relation to the properties of the dried colloid from which the solvents have been eliminated by drying. The dried colloid, however, presents difficulties in assessing its physical properties. One method of determining its toughness has been mentioned, and determinations of hardness by the Brinell method, of breaking strain, or of resistance to crushing have been applied, but not so far with much that is

informative. One method may be mentioned by means of which variations in the viscosity of the hard colloid may be traced. If large cords be pressed from different composition of the cordite type in which the proportion of guncotton to nitroglycerine is varied, these cords retain a small proportion of the volatile solvent. If now the quantity of this solvent be determined in different concentric zones it is found that as the nitrocellulose becomes dominant, a proportion is reached when the distribution of the volatile matter is no longer uniform but increases regularly from skin to core, the ratio of the content of volatile matter in the different regions remaining constant although the total quantity is reduced in the process of drying. This resistance to the migration of the solvent is some measure of the viscosity of the horny substance, and its regional determination might, perhaps, assist in the investigation of the physical condition of other hard colloids.

It is hoped that the above will show the importance of the application of the investigation of the colloid solutions of nitrocellulose and indicate, perhaps, points of theoretical interest that remain to be followed up.

*THE VISCOSITY OF SOME CELLULOSE ACETATE SOLUTIONS

BY

GUY BARR, B.A., D.Sc., AND L. L. BIRCUMSHAW

Summary.—Experiments are described which were made to investigate the changes in viscosity and density of cellulose acetate solutions in acetone on the addition of varying quantities of water, alcohol, and benzene.

In the manufacture of non-inflammable dopes used for tautening the fabric on the wings of aeroplanes, the viscosity of the solution of cellulose acetate in the dope solvent not only limits the concentration which it is possible conveniently to employ, but also necessitates the use of an acetate which does not possess the maximum viscosity in acetone solution, *i.e.*, which is more "degraded" and has less film strength than the best acetate that can be manufactured.

It has long been known that the solubility of cellulose acetate in acetone and the viscosity of the solutions is modified considerably by small quantities of water; but accurate determinations of the extent of this influence have been, up to now, lacking. It was, therefore, thought advisable to study the viscosity concentration (*i.e.*, concentration of water) curve for a 5 per cent. solution of a typical acetate in pure acetone up to the point of precipitation of the acetate. Very interesting results were obtained and it was decided to investigate the influence of benzene and ethyl alcohol (other liquids used in the manufacture of dope) in a similar manner.

Materials used and their Purification.—The cellulose acetate used was "Dreyfus" material, obtained from the Royal Aircraft Establishment in 1914.

Acetone.—This was purified by the method described by Werner and Shipsey, *J.C.S.*, 1913, 1255, and the boiling point of the final material was $56^{\circ}\cdot5$ C.

Benzene.—The benzene was purified by freezing and then by fractionation.

Ethyl Alcohol.—This was dried over quick-lime and fractionated.

Method of making Solutions.—The acetate was dried until the weight was constant and rapidly transferred to a weighed and corked tube. The cork was covered with tinfoil to protect it from the action of the liquid. Measured quantities of the acetone and water, benzene, or alcohol were then added, and the weight of each determined. The mixture was shaken thoroughly from time to time until dissolved, and then allowed to settle for at least one week.

Determination of the Densities.—The densities were determined in a small bulb pycnometer (capacity, 16 c.c.) fitted with a cap. The solution was forced from the containing tube into the pycnometer by compressed air, until the latter was fitted to just above the mark. The pycnometer with its contents was then placed in the thermostat

* The work described in this paper was carried out for the Advisory Committee for Aeronautics, to whom the results were communicated in 1919.

at 25° for 20 to 30 minutes; the solution adjusted to the mark and the pycnometer and its contents weighed.

Owing to the very viscous nature of the solutions this method was not susceptible of any great accuracy, and for this reason the specific gravities at 25° C. were not converted to densities nor corrected for the buoyancy of the air.

The viscosities were determined in an ordinary "U" form of Ostwald viscometer with suitably wide capillary. The solutions were forced by air pressure into the instrument, and the latter placed in the thermostat for 30 minutes, when the time of flow was taken with a stop-watch reading to $\frac{1}{5}$ seconds. The dimensions of the viscometer were such that a pure sucrose solution of density D_4^{25} 1.25225 had a time of flow of $48\frac{2}{5}$ seconds. According to the experiments of Heber Green (*J.C.S.*, Vol. 93, 1908, 2023), this has a viscosity of 0.2040 C.G.S. units.

The thermostat employed was of the Lowry pattern and the temperature could be kept constant to 0°.020.

The results are tabulated below :—

TABLE 1
Acetone-Water Solutions

Per cent. Water.	Mol. per cent. Water.	Density.	Time of Flow (secs.).	d × t.
0.0	0.0	0.8090	325	263
0.64	2.14	0.8106	249	202
1.10	3.66	0.8123	208	169
2.34	7.56	0.8135	155	126
2.46	7.95	0.8169	152	124
2.66	8.53	0.8167	145	118
3.90	12.15	0.8200	131	107
4.98	15.20	0.8249	122	101
6.56	19.35	0.8278	115	95
7.66	22.70	0.8478	138	117
9.50	26.80	0.8364	147	122
14.12	36.68	0.8522	160	136
18.42	43.70	0.8641	197	170
24.02	52.20	0.8803	255	224
29.00	58.70	0.8930	320	286

TABLE 2
Acetone-Benzene Solutions

Per cent. Benzene.	Mol. per cent. Benzene.	Density.	Time of Flow (secs.).	d × t.
1.33	1.05	0.8106	330	266
2.43	1.93	0.8115	363	294
4.95	3.95	0.8117	394	320
9.65	7.73	0.8175	428	350
14.50	11.75	0.8217	500	411
18.70	15.50	0.8278	626	519
24.20	24.20	0.8326	1,015	845
33.10	33.10	0.8414	2,049	1,724

TABLE 3

Acetone-Ethyl Alcohol Solutions

Per cent. Alcohol.	Mol. per cent. Alcohol.	Density.	Time of Flow (secs.).	$d \times t.$
0.51	0.68	0.8096	329	266
2.59	3.42	0.8097	249	202
5.18	6.16	0.8094	180	146
10.28	13.35	0.8104	180	146
15.74	20.20	0.8123	172	140
20.26	25.42	0.8123	169	137
24.88	31.30	0.8127	165	134
30.22	37.70	0.8128	165	134
37.96	45.60	0.8147	185	151

The next mixture made up after the last one in each of the tables contained from 5 to 10 per cent. more of the added liquid, and in each case caused precipitation of the acetate.

The curves obtained for the three liquids are very different. Thus benzene causes a progressive increase in viscosity with increased percentage of precipitant, whereas water and ethyl alcohol show an initial fairly rapid fall. It is proposed to extend the list of liquids used, and to investigate in more detail the curves in the region of precipitation. Since other types of acetate may be expected to show different phenomena, some of the curves will also be determined for solutions of cellulose acetate of different manufacture and possessing other characteristics; in addition, other concentrations of acetate will be examined.

THE VISCOSITY OF SOME CELLULOSE ACETATE SOLUTIONS.

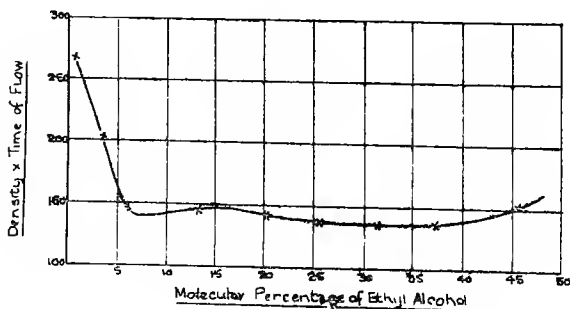


FIG.

THE VISCOSITY
OF SOME
CELLULOSE ACETATE SOLUTIONS

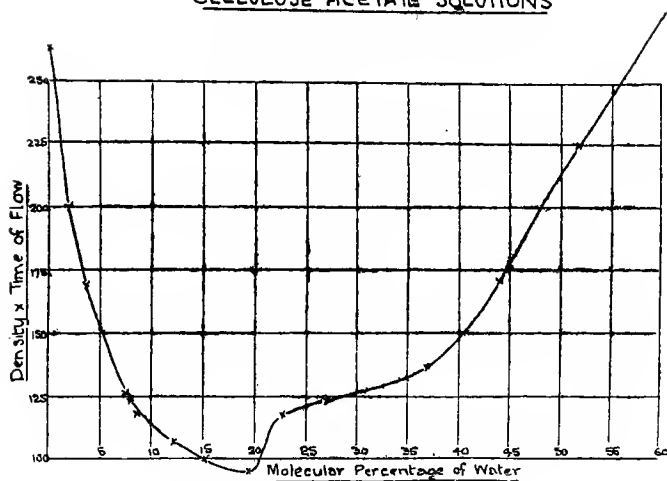


FIG. 2

THE VISCOSITY
OF SOME
CELLULOSE ACETATE SOLUTIONS.

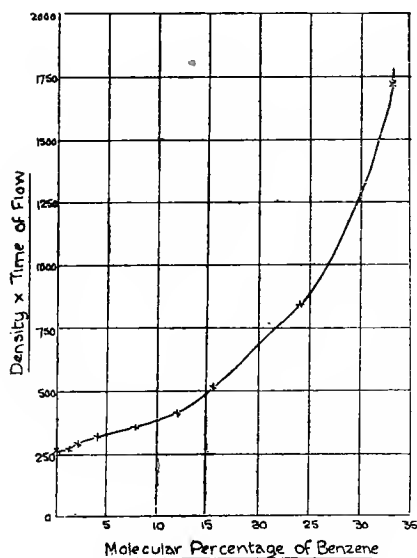


FIG. 3

NON-AQUEOUS COLLOID SYSTEMS WITH SPECIAL REFERENCE TO NITROCELLULOSE

BY

F. SPROXTON, B.Sc., F.I.C.

Nearly all nitrocellulose solvents contain the carbonyl group —CO— in the form of a ketone, ester, or acetyl group. There are, however, some exceptions, and ether-alcohol is one of considerable importance, particularly in view of its extensive use during the war in cordite manufacture. Baker¹ investigated the viscosity of ether-alcohol mixtures and concluded that dissociation of (associated) alcohols takes place in such mixtures, but is accompanied by the formation of an ether-alcohol complex, to which the solubility of nitrocellulose is due. Quite recently, Gibson and McCall² have investigated the effect of variations in the proportions of ether and alcohol on the viscosity of ether-alcohol solutions of nitrocellulose. They find that "the optimum solvent for a nitrocellulose depends on its nitrogen content, and that the higher the nitrogen content, the more ether the optimum solvent requires." This method of expressing the result is, perhaps, open to criticism. The composition of the optimum solvent may vary with the nitrogen content, but it may be directly governed by some other factor which usually varies at the same time as the nitrogen content. The variable factors in nitrocellulose are: (1) the structural complexity of the original cellulose; (2) the complexity of the cellulose after nitration; (3) the percentage of nitril groups; (4) the percentage of free hydroxyl groups; (5) minor functions such as ketonic or aldehydic groups, and sulphuric acid esters. It is possible that the free hydroxyl groups have a considerable influence on the solubility relations. Dry nitrocellulose absorbs moisture from a damp atmosphere. In fact, Will,³ in 1905, came to the conclusion that the sum of nitrogen percentage plus water absorbed was a constant (14.6). This conclusion was based on the examination of 65 samples of nitrocellulose. Macdonald's observations on the composition of the spent acids from the displacement process⁴ are best explained by assuming slight hydrolysis of the nitrocellulose when the nitrating acids are displaced by water. Now, it has been shown by Renker⁵ that cellulose dried by alcohol retains traces of alcohol even when dried at 130° C. It is not impossible, therefore, that the free hydroxyl groups in nitrocellulose attract alcohol molecules which would otherwise take part in the formation of the solvent complex, and the variations in the composition of the optimum ether-alcohol solvent for various nitrocelluloses may be due to the differences in the percentage of hydroxyl groups which the nitrocelluloses contain. A simple calculation will show that (1) if Will's generalisation is correct, (2) if the hygroscopicity of nitrocellulose is a measure of its free hydroxyl content, and (3) if the free hydroxyls withdraw alcohol from the ether-alcohol mixture, the results found by Gibson and McCall are *qualitatively* in agreement with the theory that the solvent action of ether-alcohol is due to the formation of a definite ether-alcohol complex. Baker's theory is not, therefore, definitely disproved by Gibson and McCall's observation. Chandelot, in 1912⁶, investigated the interesting fact that

moist nitrocellulose is more soluble in ether-alcohol than dry. Masson and McCall⁷ have recently published a paper on the viscosity of nitrocellulose in mixtures of acetone and water, showing that the minimum viscosity is obtained not with dry acetone, but with acetone containing a small percentage of water, varying, for instance, from 8 to 10 per cent. for a sample of nitrocellulose containing 12.3 per cent. of nitrogen, and from 6 to 7 per cent. for a sample containing 13 per cent. of nitrogen. Here, also, there is a suggestion that the free hydroxyl groups of the nitrocellulose modify its solubility relations, and that what really passes into solution is nitrocellulose + water molecules attracted by its free hydroxyl groups. In the case of dilute solutions, *e.g.*, where the concentration of nitrocellulose is about 0.1 per cent., in technically pure acetone (not specially dried), a minimum viscosity is not found as the water content increases. There is a continuous rise to a maximum value and then a fall as the solution is converted to a suspensoid sol. If a minimum occurs, it must be at a lower concentration of water than that normally present in technically pure acetone. It seems probable that in these aqueous-acetone solutions of nitrocellulose we have nitrocellulose present in all degrees of state from emulsoid to suspensoid, and this suggests the question whether it is possible, in the same solution, for emulsoid nitrocellulose to act a protecting colloid to suspensoid nitrocellulose. Mardles, Moses and Willstrop⁸ note that water, up to 6 per cent., increases the solvent power of acetone for cellulose acetate, and their paper contains a great deal of interesting information about this cellulose ester. One of their methods of investigation involves the determination of "transition temperature," *i.e.*, the temperature at which a non-solvent for cellulose acetate becomes a solvent. Since there are many transition temperatures, this might be called the Tyndall point. If a solvent is diluted by an indifferent non-solvent, such as petrol, the transition temperature is raised, and by extrapolation a value can be found for the transition temperature of the petrol. This value is artificial, because it is frequently far above the decomposition temperature of cellulose acetate, but it is useful as an index of solvent power. In the case of many binary mixtures, it is found that the curve connecting the composition of the mixture with the transition temperature shows a minimum. Such results are, of course, parallel to those obtained for the viscosity of the nitrocellulose in ether-alcohol, and it is interesting to note that the authors find that the minima in the cases of tetrachlorethane and alcohol, butyl formate and alcohol, methyl benzoate and alcohol, approximate very closely to mixtures in simple molecular proportions, which, again, suggests that the solubility is due to the formation of a molecular complex in such mixtures of substances which are themselves non-solvents.

In a contribution to the third British Association Report on Colloid Chemistry, I have mentioned another method of investigating such binary mixtures, which consists in making use of a nitrocellulose of incomplete solubility, and determining the percentage dissolved by various mixtures of the liquids under examination. Alcohol and toluene show a maximum solvent power for the samples of nitrocellulose tested, at a concentration corresponding closely to three molecules of alcohol to one molecule of toluene. The toluene and acetone solubility curve shows no maximum, the solvent power of the mixture decreasing continuously as the percentage of toluene increases. The addition of a constant percentage of petroleum spirit

to alcohol and toluene does not appear to alter the position of the optimum ratio of alcohol to toluene, but reduces the solvent power throughout the curve. The same method has been applied to investigate the solvent powers of mixtures of alcohol and tetrachlorethane for acetyl cellulose. Almost complete solubility has been obtained in mixtures containing between 20 and 60 per cent. of alcohol. It should be observed that this method is not nearly so sensitive as the viscosity method, and less sensitive than the transition temperature method of studying solvent power, but it has some technical advantages. To sum up, the solvent power for cellulose esters can be studied by the following methods:—

(1) Viscosity determinations, the assumption being that that solvent is the best which gives solutions of lowest viscosity.

(2) Determination of transition temperature, *i.e.*, the temperature at which a liquid or mixture of liquids becomes a solvent.

(3) Determination of the amount of an indifferent diluent which may be added to a solution before precipitation takes place.

(4) Determination of the amount dissolved from a sample of cellulose ester of incomplete solubility.

It would be premature to say whether these four methods all lead to the same result, but I have not found any contradictory results up to the present.

Duclaux and Wollman,⁹ by the fractional precipitation of an acetone-solution of nitrocellulose by means of water or aqueous acetone, have separated it into fractions of widely different viscosities, although of constant nitrogen content. Since the treatment is equivalent to treating nitrocellulose with aqueous acetone of varying water content, presumably the latter treatment would also fractionate nitrocellulose in this way, and it may be that method (4), given above, has this effect. With regard to the actual peptisation of nitrocellulose, there is little to add to Bancroft's report in the second British Association Report. Masson and McCall,⁷ commenting on the variations of viscosity with time in the case of solutions of nitrocellulose in ether-alcohol and in acetone, remark that two processes appear to be at work: (1) the absorption of solvent by nitrocellulose, accompanied by dispersion of the resulting gel; (2) a change in the already dispersed gel, perhaps in the state of aggregation, not necessarily accompanied by alteration in percentage composition. I have occasionally noticed evidence of the two phenomena mentioned in (1) when preparing nitrocellulose solutions. If, for instance, celloidin (a special form of nitrocellulose in small cubes) is covered with a mixture of 80 per cent. alcohol and 20 per cent. acetone and allowed to stand, after a few days one sometimes notices the formation of two boundaries. The lower one, which is separated from the core of still unswollen nitrocellulose in the centre of the cubes, is usually undulating (corresponding to the original surface of the solid celloidin), and is sharply marked by a difference in refractive index from the supernatant liquid. A few millimetres above this will be seen a horizontal layer, often marked by a layer of fine dust which has fallen through the solvent and been stopped by the slowly-diffusing viscous solution. The lower layer is evidently the boundary of the swollen gel, the upper layer the limit of the dispersion process. The fact that the upper layer is horizontal shows that the viscosity of this phase is low enough to allow relative motion in the liquid.

The colloid chemistry of the manufacture of solid celluloid is complicated and difficult. Contrary to a somewhat widespread belief, at no stage of the manufacture do we deal with a sol, if we except a momentary formation at the surface of the fibrous nitrocellulose when the liquid solvent first comes into contact with it. The amount of liquid solvent employed is less than the nitrocellulose would take up in its preliminary swelling if soaked in the solvent. As a matter of interest the volume of the gel formed under these conditions depends on the concentration of the camphor solution. For example, samples of the same nitrocellulose soaked in alcoholic solutions of camphor of 20 per cent., 30 per cent., and 40 per cent. concentration gave gels in which the specific volume of the nitrocellulose was 4.4, 3.8, and 3.5 respectively.

Since the product of preliminary swelling is a gel, it follows that the whole of the manufacture of solid celluloid from nitrocellulose deals with the gradual transformation of a gel to a solid. This transformation is accomplished by loss of solvent, which involves loss in weight and in volume, while undoubtedly the mechanical properties of the finished material are influenced also by the amount and character of the manipulation it receives in the plastic state. I have given in the British Association Report some information about the ratio loss of weight/loss of volume in the seasoning process. Since the range of density of all possible solutions of alcohol and camphor at ordinary temperatures is very small, it is interesting to find that the value of the ratio falls within this range. In the seasoning process, the loss of solvent is rapid at first, but a skin of harder and denser celluloid forms on the surface, and seasoning becomes progressively slower as this skin increases in thickness. With moderately thick sheets (*e.g.*, 1 cm. and over) even after the loss of weight has become inappreciable, the centre of the celluloid is softer than the outside, and this fact must be taken account of in any investigation of elasticity, since the usual mathematical theory assumes homogeneity of the material. If a rectangular prism of moderately thick seasoned celluloid is sliced down the middle, each piece will assume a curve with the new surface concave, owing to the escape of solvent and consequent shrinkage. A cube of celluloid of 3-in. side made many years ago, and now in use as a paper-weight, shows a lens-shaped bubble inside where the soft core has gradually shrunk away from the hard outer shell. The final material is usually regarded as a solid solution of camphor and nitrocellulose, but the traces of alcohol which are retained probably form an integral part of the system. The reasons for the plasticity of celluloid when warm (one of its most valuable properties) lead to interesting speculations. Nitrocellulose has no melting point, since it decomposes before this point is reached. Camphor melts at 182.5°C . Celluloid becomes appreciably plastic at 80°C . Therefore the melting point, if the term may be allowed, of the mixture is greatly below that of either constituent. The traces of alcohol present no doubt have a considerable influence in reducing the melting point further than would be the case with camphor and nitrocellulose alone. It may be noted in passing that camphor forms liquid mixtures with several solid substances at ordinary temperatures, and possibly this is one of the properties which make camphor adaptable for celluloid manufacture. Most of the substances which have from time to time been used as camphor substitutes have had much lower melting points than camphor, but the celluloid made from them does not usually become-

plastic at a lower temperature on that account. It would appear, therefore, that the plasticity of warm celluloid is determined not by the melting point of the solid solvent, but by the properties of the complex solid solution formed by nitrocellulose, solid solvent, and liquid solvent. When experimenting with unusual materials, one sometimes encounters limits to the mutual solubility, and the phenomenon occurs known in the industry as "exudation." Mardles, Moses, and Willstrop⁸ mention occasional cases of crystallisation on acetyl cellulose films. This separation of the solid solvent no doubt depends on its solubility in the liquid solvent and in the nitrocellulose, and it would be an interesting phase rule study, although of great experimental difficulty. I have not seen it occur with camphor, probably because of (1) the high mutual solubility of camphor, nitrocellulose, and alcohol; (2) the high vapour pressure of camphor, at ordinary temperatures, which would cause the camphor to volatilise immediately. Probably it could be tracked in the case of camphor by searching for a break in the seasoning process, using a sample of unusually high camphor content.

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- ¹ Baker, *Trans.*, 1913, 653.
 - ² Gibson and McCall, *J.S.C.I.*, 1920, **39**, 172T-176T.
 - ³ Will, *Mitt. Centralst. f. Wiss. Tech. Unters*, Berlin, 1904, No. 4, 1-33.
 - ⁴ Macdonald, *J.S.C.I.*, 1911, **30**, 251.
 - ⁵ Renker, "Ueber Bestimmungsmethoden der Cellulose" (Berlin University, 1909; *Analyst*, 1910, 35, 71).
 - ⁶ Chandelon, *Bull. Soc. Chim. Belg.*, 1912, 26, 495-506.
 - ⁷ Masson and McCall, *Trans.*, 1920, **117**, 819-823.
 - ⁸ Mardles, Moses and Willstrop; Advisory Committee for Aeronautics; Reports and Memoranda, No. 568.
 - ⁹ Duclaux and Wollman, *Bull. Soc. Chim.*, 1920, **27**, 414-420.
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THE ACTION OF LIGHT AND OXYGEN ON RUBBER

BY

B. D. PORRITT, M.Sc., F.I.C.

The prejudicial effects of light on rubber, technically known as "perishing," attracted the attention of Thomas Hancock nearly 100 years ago, and as a result of experiments, he found that by blackening the surface of the rubber, deterioration could be prevented ("Origin and Progress of the India Rubber Manufacture," London, 1857, p. 29). The deleterious effect on the rubber proofing of certain dressings present in dyed fabrics—presumably metallic mordants—was remarked, as also was the fact that the non-caoutchouc constituents of the rubber exercised a marked protective influence (*ibid.*, p. 32).

With the introduction of the telegraph some 30 years later, and the employment of gutta percha for insulating purposes, attention again was directed to the subject owing to the numerous cable failures which initially occurred, and a Joint Committee of the Privy Council for Trade and the Atlantic Telegraph Co. was appointed to report on the matter.

As a result of investigations carried out at the instigation of this Committee and the Director of Indian Telegraphs, it was found that (W. A. Miller, *J. Chem. Soc.*, 1865, **18**, p. 273; A. W. Hofmann, *J. Chem. Soc.*, 1860, **13**, p. 87) the alteration took place only on exposure to air and light when an alcohol soluble oxidation compound, termed in the case of rubber "Spiller resin" (J. Spiller, *J. Chem. Soc.*, 1865, **3**, p. 44) was formed. It was further suspected that this change was promoted by contact with copper (*see* W. Thomson and F. Lewis, *Proc. Manchester Lit. and Phil. Soc.* (4) **4**, April 1891). No further material contribution was made to the subject until recent years, when the question of "tackiness" in raw rubber began to receive attention. It was found by D. Spence (*Quarter Century No. I.R.J.*, 1909, p. 43) that while "tacky" rubber was characterised by possessing a low solution viscosity compared with the normal material, no difference could be detected in chemical composition; while E. Fickendey (*J. Chem. Ind. Kolloids*, 1911, **9**, p. 81), by exposing rubber to sunlight in tubes containing air and other gases, proved that the presence of oxygen was necessary before this defect could develop. These two important observations were later confirmed by A. Van Rossem (*Rubber Industry*, 1914, p. 149) and K. Gorter (*Le Caoutchouc et la Gutta Percha*, 1915, **12**, 8,724).

In 1906 an attempt by Herbst (*Ber.*, 1906, **39**, p. 523) to determine the composition of the products formed by the action of air on a hot solution of rubber in benzene resulted in the preparation of three different substances, one a viscid syrup constituting the main product, having a composition approximating to $C_{10}H_{16}O$, and the other two resinous compounds with a higher oxygen content corresponding to $C_{10}H_{16}O_3$, one being an amorphous powder and the other a brittle solid. Passing reference might also be made to the important work of C. Harries on the products formed by the action of ozone on rubber.

Hitherto no attempt appears to have been made to study the progress of the oxidation of rubber by any accurate quantitative method, and it was left to Peachey in 1912 (*J.S.C.I.*, 1912, p. 1103) to supply this omission.

By determining the rate of absorption of oxygen by a thin film of rubber deposited on the interior surface of a flask heated to 80° C., it was shown that initially little chemical change took place, a period of rapid oxidation then set in, slowly diminishing as the reaction neared completion, when the amount of oxygen taken up corresponded with the formula $C_{10}H_{16}O_4$. The removal of resin was found to considerably hasten the start of the reaction.

It was pointed out by Wo. Ostwald (*J.S.C.I.*, 1913, p. 179) that the graph obtained by plotting Peachey's results was of the type characteristic of autocatalytic reactions—an analogy which is supported by the suspicion that traces of peroxides are formed during the process of oxidation.

In a further communication (*J.C.S.I.*, 1918, 55T), Peachey and Leon showed that the removal of moisture exerted no effect on the rate of oxidation, that balata differed from rubber both in regard to the rate of the reaction and in the final product containing a higher proportion of oxygen, and they further demonstrated that a proportion of CO_2 was formed during the reaction at the somewhat elevated temperature employed. In connection with this last observation, it is surprising that none of the published investigations dealing with the perishing of rubber contains any reference to the pungent acid odour which, under ordinary conditions, is a well-marked feature of the change equally with rubber, gutta percha, and balata. (See, however, H. P. Stevens, *J.S.C.I.*, 1919, p. 196 T.)

We may now, perhaps, turn for a moment from the scientific to the technical aspect of the question, more particularly in connection with the manufacture of balloon fabric, which probably represents one of the earliest uses—apart from erasers—to which rubber was put (see *Mechanics Magazine*, 1836, XXIV., p. 529—The "Coronation" Balloon Lost off Beachy Head, 1822).

It was generally recognised that it was to the ultra-violet region of the spectrum that the deleterious effects of light on rubber must be attributed, and consequently in order to protect material exposed to drastic weathering, some absorbent screen was desirable, as had been shown many years before by Hancock. The methods initially employed were either to dye the outside ply of cotton yellow (Porritt and The North British Rubber Co., Eng. Pat., 1972/1913) or to protect the outer surface with a light layer of rubber pigmented yellow or red.

The use of rubber compounds containing heavy metals such as litharge (Porritt and The North British Rubber Co., Eng. Pat., 11743/1912) or aluminium powder, was also suggested. While these methods of protection were reasonably adequate for the conditions which obtain in temperate climates, they failed to satisfy the demands imposed by the intense radiation experienced in tropical countries, and when, therefore, a call arose during the War for aeronautical equipment for the East, a novel situation had to be faced. Two types of protection have been found to give satisfactory results under such conditions. The one (J. H. Mandleberg and J. Mandleberg & Co., Eng. Pat., 124495/1919) which involves the employment of small proportions of litharge and other ingredients amongst the proofing mixing probably depends mainly on the formation in the

rubber of lead sulphide in a colloidal form—a phenomenon which has been previously noted (Lewis and Waumsley, *J.S.C.I.*, 1912, p. 518).

The other, which has been termed the “molecular protection process,” (Wheatley and The North British Rubber Co., Eng. Pat. 5915/1915) involves the selective absorption of the ultra-violet light by a suitable coloured organic compound actually dissolved in the rubber.

By the use of either of these two methods, especially if combined with some of the earlier protective processes, it is probable that at present the determining factor for the life of a balloon envelope in the tropics is the durability of the textile rather than that of the rubber.

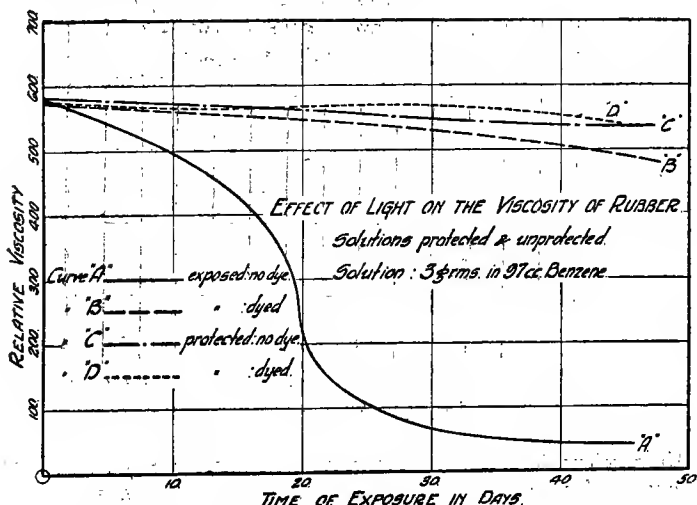
This brief digression may serve as an explanation for, and introduction to some experiments carried out in connection with the second of the two protective processes just described.

As it was known that the viscosity of rubber solutions was rapidly reduced by exposure to light, it was thought that this might afford a more rapid method of judging the protective efficiency of different rubber-soluble colouring matters than the customary balloon fabric outdoor exposure test, which, in a northern climate, is at all times a tedious process, and particularly so during winter months.

As will be evident from the Graph No. 1, which represents the behaviour of a benzene rubber solution with and without Sudan III. (composition : 3 grammes masticated rubber, 0.06 grammes Sudan III., 97 c.c. benzene), the method gives very striking results, indicating that the change of viscosity experienced by rubber solutions exposed to light is to be attributed to that portion of the incident radiation having an oscillation frequency greater than 2,000.

Some preliminary experiments on the absorption spectrum of a specially purified caoutchouc-ether solution made by S. J. Lewis and the writer point to the light absorption in this region being of a general character. (*J.S.C.I.*, 1921, 618 T.)

GRAPH I



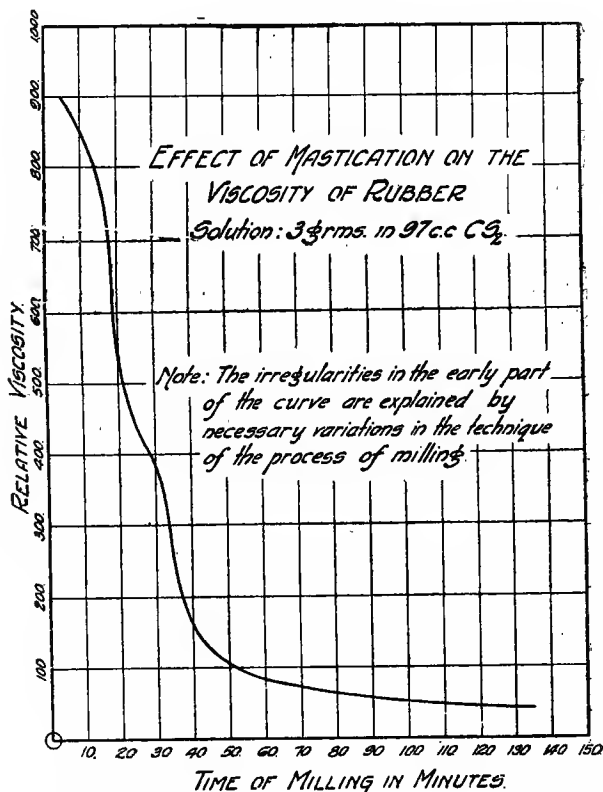
That the function of the dye is probably that of a light filter only, and not a catalyst, was shown by exposing to light three bottles

containing rubber solution suspended in jars full of benzene. To the first no dye was added; in the second the solution was coloured by the addition of sudan III., while in the third an equivalent amount of this colour was added to the surrounding benzene. The viscosity changes over a period of two months were as follows:—

	Unprotected.	Protected Internally.	Protected Externally.
Initial Visc.	548.7	548.7	548.7
31 days exp.	52.5	457.0	473.2
60 days exp.	30.2	339.2	393.5

This investigation was subsequently extended in other directions. As is generally known, the process of "mastication," which forms an essential preliminary process in the preparation of rubber for factory use, is also characterised in its initial stages by a remarkable diminution in the solution viscosity of the rubber. This will be evident from the following curve:—

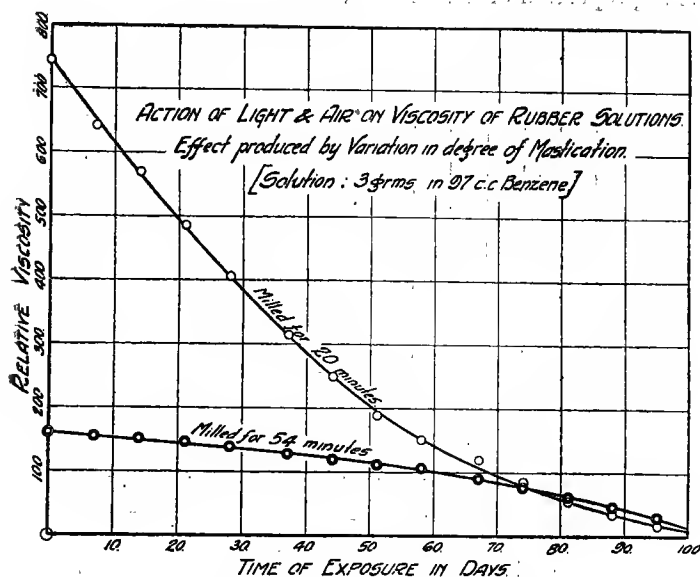
GRAPH II



With a view to determining whether the changes produced by the process of mastication had any effect on the susceptibility of raw rubber to light, a range of samples was obtained throughout the operation, and from these solutions were prepared and exposed, the viscosities being determined at intervals. The results would

suggest that the physical changes produced in rubber by mastication are not necessarily the same as the initial effects arising from exposure to light and air, and that the stability to light may increase rather than diminish with the severity of the treatment, though this is at variance with the results of Weber, who found that overmilled rubber was prone to oxidation. (C. O. Weber, *I.R.J.*, 1903, 25, p. 639.)

GRAPH III



In conjunction with the foregoing experiment, a duplicate set of solutions was retained in the dark and tested in non-actinic light. The results, which need not be quoted in detail, showed in most instances little or no change whatever after several months' storage. In the case of the samples of higher viscosity, however, a slight increase was indicated. The behaviour of the rubber itself on keeping in the dark at ordinary temperature was accordingly examined, and some of the results obtained are shown on the following graph (*see next page*).

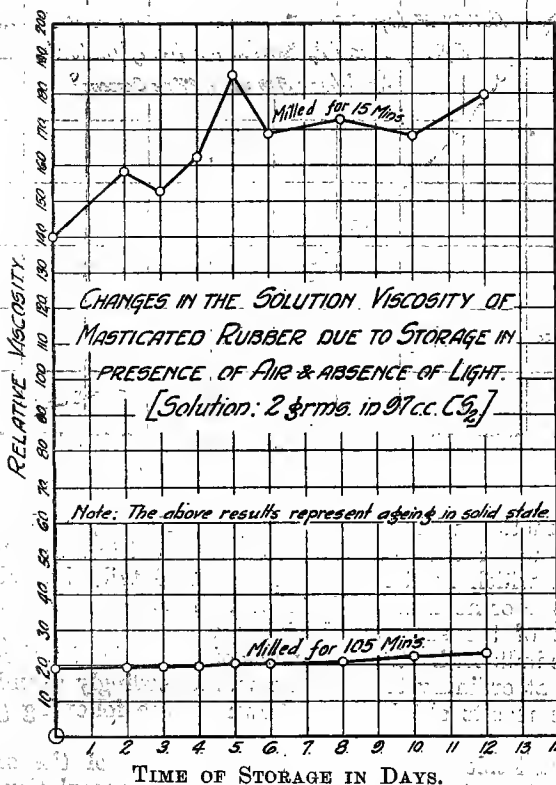
The remarkable irregularities in the results of the samples of higher viscosity at first gave rise to much speculation, but on investigation it was found that the viscosity of the surface material exposed to air was much lower than that in the interior of such samples, from which it reasonably may be inferred that the presence of oxygen tends to inhibit the "regain" characteristic of under-masticated rubber.

Before making any generalisation regarding the preceding observations, it is desirable to draw attention to the fact that the action of light and air on rubber is not always associated with ill-effects. In the early days of the industry, exposure to sunlight—a process termed "solarisation"—was frequently employed to produce a type of surface vulcanisation (Charles Goodyear, "Gum Elastic," New Haven, 1855, pp. 93 and 113, also Thomas Foster, Eng. Pat. 10092/1844), and this primitive method still appears to be employed

by the native tribes of South America for the production of crude articles for their own use.

A comparatively recent development of this old process involves the use of light sources rich in ultra-violet (Helbronner and Bernstein, *Le Caoutchouc et la Gutta Percha*, 1915, 12, 8720) for the production of "solutions" of vulcanised rubber, and under the influence of a quartz mercury vapour lamp, a solution of rubber and sulphur undoubtedly rapidly sets to a stable "gel" accompanied by the combination of a small proportion of the sulphur.

GRAPH IV



Under ordinary daylight conditions it is found, however, that the addition of sulphur to a rubber solution, if anything, accelerates the rate of viscosity diminution, and it was consequently thought of interest to see whether the removal of oxygen would enable the sulphur to respond to the more feeble, incident radiation. An experiment in this direction did not, however, produce the anticipated result, those solutions to which crystalline sulphur had been added showing no apparent change after several months exposure, while the blank sample containing rubber only, after a few days suddenly set to a "gel" without any obvious preliminary increase in viscosity. This "gel," moreover, on exposure, was found to be rapidly transformed to a liquid.

It is hoped shortly to design a viscometer which will enable these peculiar changes to be studied more thoroughly, using specially purified materials in view of the marked effects produced by traces of acid (Spence and Kratz, *Z. Chem. Ind. Kolloids*, 1914, 14, p. 262), and to verify Van Rossem's statement that, even in the absence of air, the action of light results in a reduction in the viscosity of rubber solutions.

While it would appear likely that the presence of air is not favourable to the light vulcanisation effect, it must be noted that in the nascent condition, oxygen is itself capable of producing a similar result, since organic peroxides which have recently been put forward as vulcanising agents (I. I. Ostromisslensky, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 1467) have been proved in a measure to function as such (H. P. Stevens, *J.S.C.I.*, 1917, 107).

Finally, it may be of interest to draw attention to the important, but generally unrecognised, effect which is produced in the vulcanisation of rubber by the agency of sulphur and heat when this process is carried out in the presence of air. Those familiar with the early history of the industry may recall the fact that Goodyear's discovery of this remarkable transformation was due to the accidental heating of a piece of rubber containing sulphur and white lead either before or on a hot stove. Hancock, when independently endeavouring to obtain the same result, secured no success by heating samples containing rubber and sulphur alone, and ultimately discovered that to effect the change desired it was necessary to immerse the rubber in molten sulphur.

Technical experience has confirmed these early observations and proved that with sulphur only the absence of air is necessary to ensure vulcanisation, while to secure satisfactory results by the "dry heat" process, the use of a positive catalyst such as litharge, in addition to sulphur, is indispensable.

Comparatively little is known regarding the mechanism of the changes which take place during the perishing of vulcanised rubber, beyond the fact that the final products resemble those of raw rubber in properties and composition, that oxidation takes place in the absence of light if the material has been over-vulcanised and is probably promoted by the presence of various catalysts.

Recent work, however, has shown that marked alterations take place on ageing in the tensile properties of over-vulcanised rubber prior to oxidation setting in (*Annual Report on the Progress of Applied Chemistry*, 1919, p. 338), and it is possible that in this preliminary physical change oxygen is again functioning as a catalyst—a suggestion which is now under investigation.

The preceding résumé of the information which is available on the effects produced on rubber by light and oxygen acting either together or independently, may be summed up briefly under the following headings :—

(a) Under ordinary conditions the action of light and oxygen would appear to take place in two stages, the first being an alteration in the state of the molecular aggregation during which oxygen functions mainly as a catalyst, and the second a series of chemical reactions in which the active participation of oxygen is promoted by the formation of an auto-catalyst—probably a peroxide.

(b) The development of the former alteration which constitutes "tackiness" is probably further promoted or retarded by other

catalysts, while the final transformation into resinous compounds of indefinite composition known as "perishing" is possibly affected by an entirely different set of activating and inhibiting agents.

(c) Though the reduction in the solution viscosity which characterises the first effects of light and oxygen on rubber can be reproduced by the application of either heat or mechanical working in the cold, it is doubtful whether the changes thereby produced in the rubber are in other respects analogous.

(d) In the presence of sulphur and under the influence of a light source rich in ultra-violet, in place of "depolymerisation," a change resembling vulcanisation is induced.

(e) In the absence of air, "tackiness" will not develop in the solid as a result of exposure to daylight, while a benzene-rubber solution under similar conditions sets to a "gel" which liquifies on re-exposure to air.

(f) In the absence of actinic light, rubber, either solid or in solution, undergoes no reduction in viscosity as a result of exposure to air, but if previously submitted to a limited amount of mastication, tends to regain its initial properties. This change is, however, partially inhibited by oxygen.

(g) The efficiency of sulphur as a vulcanisation agent, unless supplemented by the presence of an appropriate accelerator, is neutralised by the presence of oxygen.

(h) Under certain conditions oxygen would appear capable of assuming the function of a vulcanising agent.

In considering the foregoing summary of the work in connection with the changes resulting from the action of oxygen and light on rubber, it will be well to remember that the little which is known is either related to chemical properties or else to one physical characteristic, namely, viscosity.

It is hardly likely that an obviously complex series of changes can be completely elucidated in so simple a manner, and the results of a careful study of other physical properties must be awaited before a definite understanding is reached.

For the moment it will suffice to say that next to sulphur, oxygen is probably the most important rubber catalyst, and that its effects must be carefully considered at all stages from the photo or bio-synthesis of caoutchouc in the latex to the final transformation of rubber into a manufactured product.

In conclusion, the writer has to express his obligation to the North British Rubber Co., Ltd., for their permission to make use of some results obtained in the course of work carried out in their research laboratory.

British Rubber and Tyre Manufacturers' Research Association,
Chemistry Department,
University College,
London.

The following contribution to this section of the Discussion was received from **Professor Dr. Wolfgang Ostwald** (Leipzig) in response to an invitation :—

CONTRIBUTION TO THE DISPERSOID ANALYSIS OF NON-AQUEOUS SYSTEMS

BY

WOLFGANG OSTWALD (LEIPZIG)

1. *Introduction.*—Although the study of non-aqueous dispersoids is of well-recognised importance, especially in technical respect—as is proved by the selection of the subject as one of the problems for this discussion—there are only a few researches on certain dispersoid-chemical characteristics of such systems. Solutions of nitrocellulose, *e.g.*, are usually spoken of as colloidal. De Mosenthal¹ has, indeed, found that nitrocellulose solutions in acetone do not dialyse through pig's bladder and parchment paper, and that they do not exert any "osmotic" pressure. On the other hand, J. Duclaux and E. Wollman² observe distinct "osmotic" pressures and at least partial dialysis when using membranes of denitrated collodion. Still less accurate is, for instance, our knowledge of the degree of dispersions in solutions of resins, fats, oils, dyes, &c., in organic dispersion media. *Indirectly* we conclude sometimes that such systems are colloidal in nature because of the marked viscosity-concentration function, the formation of jellies or the phenomena of swelling. An exact characterisation by the classical methods of diffusion or dialysis is almost always missing, however.

The main reason for the want of such researches lies presumably in our methods. We may not, without restrictions, apply to non-aqueous systems the methods worked out for aqueous dispersoids, nor the membranes used. If we study the dialysis of acetone solutions through parchment paper, *e.g.*, we must first establish that there are, with respect to these membranes, *both* diffusing *and* non-diffusing acetone solutions. An always negative dialytic effect, as well as an always positive effect, would only show that the membrane is either too dense or too permeable for the solvent in question to admit of differentiation according to degrees of dispersity. The point is not only whether the membrane in itself possesses a gel structure; the degree of shrinkage or solvation of the membrane must have suitable mean values in the respective organic solvents.

The following is a small contribution to the methodics of dispersoid analysis for systems, the dispersion medium of which is alcohol of 96 or 97 per cent. The selection of this alcoholic concentration is not arbitrary, but the result of practical experience with alcoholic media of various concentrations. This concentration has proved to yield much more stable and more easily reproducible relations than alcohol of higher strength; the concentration is particularly interesting also in technical respect. Experiments with other dispersion media will be published on another occasion. Many years ago the author conducted experiments, not yet published, on dialysers for organosols. The experiments described in this communication are new and were made by the author in conjunction with Dr. P. Wolski.

2. *Preparation of a Stable Alcosol for Purposes of Control.*—It is very easy, it will be seen, to prepare molecularly-dispersed, *i.e.*, dialysing and diffusing alcoholic solutions, but not easy to prepare stable alcosols. On the other hand, the possibility of preparing a tolerably stable alcosol as standard liquid is presumed for the experiments to be described. Of the various alcosols tried, (Ag, $\text{Fe}(\text{OH})_3$, As_2S_3 , &c.) the *mercury sulphide alcosol*, previously prepared by A. Lottermoser, proved most suitable. We start from a solution of any concentration, including the saturated (10 per cent.) solution, of mercury cyanide $\text{Hg}(\text{CN})_2$ in alcohol of 97 per cent. (*not stronger*). A brisk current of H_2S is passed through this solution for a considerable time, say, 10 minutes. Any flakes, occasionally noticed, will be peptised again on further treatment with H_2S . A sol of dark deep-brown colour is formed; it may be diluted with alcohol of 97 per cent. and then be stabilised by further treatment with H_2S . In a closed vessel the sol may be kept for weeks; a certain excess of H_2S seems to favour stability.

The *freshly*-prepared sol, containing H_2S , may be diluted with the same volume of ether without showing any precipitate after two days. This is important for some of the experiments.

As a typical molecularly-dispersed system in alcohol of 97 per cent. *Night Blue* may be recommended, which is known as a typical colloid in water. The following arrangements for dialysis and diffusion are best tested with the mercury sulphide alcosol on the one hand, and alcoholic night blue on the other.

3. *Dialysers for Alcosols.*—Among the membranes which admit of dialytic differentiation of dispersoids in alcohol of 97 per cent. are the following:—

(a) Common Parchment Paper.

(b) Collodion Membranes. These membranes are prepared by the same method which the author recently described for the preparation of analytical dialysers for hydrosols.³ Extraction bags of paper are impregnated with 97 per cent. alcohol. Pharmaceutical collodion solution of 4 per cent. is poured into the still wet bag; the bag is quickly dried in a warm place, so as to feel dry to the touch of the finger, until the smell of ether has disappeared. The same collodion solution is poured in for the second time and the drying is renewed; the dialysers will then be ready for use.

In making use of the dialysers care should be taken to have the liquid inside and outside at the same levels; excess pressure may render these dialysers—as well as the others to be mentioned—leaky. With long standing some collodion will dissolve in the alcohol; the bags need not lose their tightness for this reason, however.

(c) *Rubber Membranes.*—The material used is a thickish ethereal solution of unsmoked crepe as formed when an excess of caoutchouc is kept standing with ether for a long time in the dark. Diluted thinnish solutions of rubber have not given good results. Exactly as with the colloid membranes just mentioned the bags are moistened with alcohol and treated and dried for periods of from 5 to 10 minutes.

(d) *Gelatine Membranes.*—The solution used was 1 per cent., aged under thymol. The preparation is as just described, except that the two drying intervals must be prolonged to 24 hours.

4. *An Alcoholic Jelly for Diffusion Experiments.*—In demonstrations of dispersoid analysis it is customary to place a layer of the solution to be tested on a suitable jelly. Especially when the systems are

coloured, it is easy rapidly to distinguish colloidal from molecularly-dispersed systems either by the penetrations of the solution into the jelly, or by the observation that the contact surface becomes indistinct. The jelly suitable for alcoholic systems is prepared from collodion by the following method:—

(a) In the first instance we may directly place pieces of nitrated cotton, e.g., the commercial *celloidin* of *Schering*, into the solution to be analysed, and then look for any penetration after rinsing the cotton and cutting it open. This gel., which is supplied in transparent blocks, is said to contain about 30 per cent. of nitrocellulose and no medium except alcohol. As a matter of fact ether is not quite absent, as the smell indicates. By repeated washing with 97 per cent. alcohol the ether may, at any rate, partly be removed; only traces of nitrocellulose will be dissolved by this operation.

Into such blocks Night Blue and Magdala Red will deeply penetrate within a few hours, whilst the HgS-sol. will not enter into the gel even in the course of days.

b) When alcoholic collodion jelly is prepared for the test-tube experiment in the usual way, the following difficulties will arise: Even solutions of collodion rich in alcohol do not gelate on cooling, nor in the course of time. The gelation takes place only with change in the concentration, and in the composition of the disperse phase. There is the further difficulty of obtaining the jellies free of ether. The following procedure has answered best: The collodion wool is disintegrated and kept standing for four or five hours with ether until it has completely dissolved. The solution is rubbed with four times its volume of alcohol and evaporated to a thick consistency at 50° or 60° C. Alcohol is again added as before, and the evaporation repeated, several times if necessary. The final solution will be a slightly turbid thickish liquid of about three times the volume of the original solution in ether (containing, therefore, 5 or 6 per cent. of nitrocellulose) faintly smelling of ether. The criterion for the "maturity" of the solution is a strong tendency to surface-skin formation. The solution is poured into test tubes and allowed to stand for 24 hours at ordinary temperature. The skin first forming will gradually thicken, but the solution underneath it may remain fluid for a long time. The formation of a skin thus imparts to the experiment the character of a dialysis, which spontaneously passes into that of a jelly-diffusion. Since the last traces of ether are retained with great persistency, the solutions to be examined should not be sensitive to ether; that is so in the case of the HgS-alcosol, as was stated above. For the demonstration of these diffusion experiments this HgS-sol and night blue in alcoholic solution may again be utilised.

5. *Some Results of Dialysis and Diffusion Experiments with Solutions in 97 per cent. Alcohol.*—It should be pointed out in the first instance that the HgS-alcosol described could neither be dialysed, nor be diffused with any of the arrangements mentioned, although it passed readily through the densest paper filters of Schleicher and Schüll, 602 e.h. The membranes and gels described were hence, without doubt, impervious to colloids. That could not be ascribed to coagulation at the membrane, although such coagulation was occasionally noticed. It was observed, on the contrary, that the sols, kept merely covered up in the collodion dialyser, or over the diffusion jelly, remained deep dark-brown for 10 days. When poured off finally the sols passed through a baryta filter without any decomposition. On the other

hand, we frequently found dialysers which were not impervious, and through which the colloid passed in a short time, yet *likewise undecomposed*. The point in question is hence actually the mechanical density of the membrane or gel, and not perhaps any chemical or colloidochemical reaction with the sol.

The dispersoid analysis of substances which are spontaneously soluble in alcohol of 97 per cent. yielded a somewhat surprising result. *So far we have not succeeded in finding any substance, spontaneously soluble in alcohol of 97 per cent., which would not dialyse and diffuse to a perceptible degree.* All the solutions so far studied are, *at least partly*, molecularly-disperse. It is presumable that, in 97 per cent. alcohol, *dispersoids of variable concentration*⁴ will frequently occur, *i.e.*, systems, the degree of dispersion of which strongly varies with the concentration, decreasing as the concentration decreases. Only in more concentrated solutions the individuals unite to coarser aggregates. We meet with similar relations in dyes, *e.g.*; at the same time these structures are also "polydisperse"; they contain both molecular aggregates and coarser aggregates, presumably in a definite equilibrium ratio.

Not all the substances enumerated below have been submitted to all the dialyser tests mentioned, although the more interesting substances were analysed by all the methods mentioned. The majority of the tests was made with the collodion and gelatin dialysers and with the collodion jellies. It should, however, be emphasised that membranes of various types gave throughout *equal* results. Substances which passed through gelatin, hardened with alcohol, passed also through collodion or rubber, &c. It should be stated also that the imperviousness of the dialyser to the HgS-sol was in most cases retested after the experiment. Whenever permeability was noticed, the experiment was repeated.

The following substances did dialyse and diffuse :—

Dyes.—Night blue, Magdala red, alkannin, cyanin, alizarine, nigrosin (faintly violet); further six different technical spirit lacquers, &c.

Iodine diffused at a strikingly rapid rate in 97 per cent. alcohol.

Of *resins* dialysed in 97 per cent. alcohol: colophony, copal, mastic, dammar, Burgundy resin, guajac, dragon's blood, &c.

The permeability test is easily made in these cases by dropping the external liquid into a beaker containing water or solution of aluminium sulphate; after dialysing for 24 hours a milky turbidity was always noticed.

Dialysis was further observed with alcoholic solutions of linseed oil, bees' wax, neutral fats (like cocoa fat), lard, &c.; further capric acid, aluminium oleate. The test is here made as first indicated with the aid of water or of a solution of aluminium sulphate. Confusion with traces of collodion, which might be dissolved by the alcohol as stated above, is easily avoided; the collodion is precipitated in films or scales, but does not give rise to a milky turbidity. It is of special interest to mention that an alcoholic albumenoid, zein, is also distinctly dialysed. This material is prepared by extracting granulated maize with alcohol of 97 per cent at 50° or 60° C., and by filtering the yellowish solution. The analytical test was, in this case, performed with the aid of the Essbach reagent (picric acid plus citric acid) after dilution with water to three or four times the volume, or with the xanthoprotein-reaction. Mere pouring into water was

not decisive since the solution might contain lipoids. Pouring of the external liquid into ether also furnishes a sensitive test. Zein diffuses, in solution in alcohol of 97 per cent., through all the following membranes: parchment paper, collodion, rubber, gelatine. In this case as well the dialysers were subsequently submitted to a test with the HgS-sol. The diffusion experiment into collodion jelly did not lead to any definite result, because zein, differing from the HgS-sol in this respect, is easily precipitated by small proportions of ether.

This dialysis of zein in 97 per cent. alcohol is of special interest because it points undoubtedly to a molecularly-dispersed condition of this albumenoid in that dispersing medium. It would be very desirable to study these solutions from the standpoint of physical chemistry with respect to true solutions, *e.g.*, by determining the boiling point at reduced pressure. So far colloid-chemists have mainly been endeavouring to transform "crystalloids" in the sense of Graham into the colloidal state. The case of zein may indicate the way conversely of transforming Graham's colloids or, more generally, substances of complex chemical composition by gentle methods into the molecularly dispersed state.

Summary

The author describes the preparation of membranes and jellies suitable for the dispersoid analysis of solutions in alcohol of 97 per cent., for both dialysis and diffusion experiments.

The mercury sulphide alcosol, the preparation of which is explained, proves to be an especially stable sol suitable for these tests.

It results that the solutions so far examined, of dyes, resins, neutral salts, fatty acids, soaps, &c., produced by the spontaneous solution of these substances in alcohol of 97 per cent., are all molecularly-dispersed or contain, at any rate, molecularly-dispersed particles in considerable proportions. Zein, the albumenoid of maize which is soluble in alcohol, is also found to be dialysable.

¹ De Mosenthal, *Journ. Chem. Soc.*, **30**, p. 782 (1911).

² J. Duclaux and E. Wollman, *Compt. Rend.*, **152**, p. 1580; *Bull. Soc. Chim.*, [4], **27**, p. 414 (1920); "*Le Caoutchouc et la Guttapercha*," p. 10579 (1920).

³ *Cp.* "*Kleines Praktikum der Kolloidchemie*," Dresden, 1920, Th. Steinkopff, p. 22.

¹ Wo. Ostwald, "*Grundriss der Kolloidchemie*," 6th edition, p. 39 (1921).

DISCUSSION

Mr. A. Highfield: It has been suggested by Mr. Sproxtton that the solvent power of ether-alcohol mixtures of nitrocellulose is due, as was originally proposed by Baker (*J.C.S.*, 1912, T. 1409), to a loosely-held ether-alcohol compound, this complex exerting a solvent power while ether and alcohol do not do so.

The recently published work of Gibson and McCall, if applied quantitatively to this suggestion, seems to render it very improbable. In the first instance, Baker's theory was based merely on certain departures on the experimental values of the viscosity of ether-alcohol mixtures from the calculated values, and can only be said to be but indicative of this ether-alcohol complex.

As regards these ether-alcohol nitrocellulose solutions, given the same concentration, the viscosity of a solution is not necessarily a criteria of the optimum solvent. In the case of solutions, the term "best solvent" implies, of course, greatest solvent power and, incidentally, a clear demarcation of the phases when saturation is reached. In these instances we do not, in general, get this latter phenomena, and it becomes, in consequence, exceedingly difficult to use the ordinary phraseology of solutions. The real meaning of this complex theory is, I take it, that the solvent power of ether-alcohol mixtures is due to this ether-alcohol complex, and that the ether-alcohol mixture which contains the greatest amount of this complex will be the best solvent and will also give the solution with the minimum viscosity. Qualitatively, this is satisfactory enough.

A more quantitative investigation, however, reveals several anomalies. It has been found that nitrocellulose solutions in ether-alcohol containing 2 per cent. of water have a comparatively constant viscosity when considered with those containing 7 per cent. of water, the ether-content being kept within the limits of 10 to 60 per cent. The variations of the former solutions are about 20 per cent. and the latter about 300 per cent. It is clear that the variation in the amount of the ether-alcohol complex is not a predominating factor.

Another consideration is the nitrogen content of the nitrocellulose. Reference to Gibson and McCall's work shows that for 4 per cent. solutions of nitrocellulose and nitrogen content 11.8, the solvent which gives the solution with minimum viscosity contains about 50 per cent. ether and 50 per cent. alcohol. The corresponding solvent for a nitrocellulose containing 12.5 per cent. of nitrogen is about 70 per cent. ether and 30 per cent. alcohol. The explanation of this on this "complex theory" is that the affinity of the former nitrocellulose (11.8 per cent.) for alcohol is greater than the latter. Consequently, in the former instance more alcohol will be required to saturate the nitrocellulose and to give the maximum amount of ether-alcohol compound than in the latter case (12.5 per cent.). This implies that a change of 0.7 per cent. in the nitrogen content of a nitro-cotton involves 20 per cent. of the alcohol in a 4 per cent. solution. It would thus seem that for more concentrated solutions very little alcohol would be available for the formation of the ether-alcohol complex, and that it would be difficult to make these solutions. This is not in accordance with experience.

Also, if the postulate that the affinity of nitrocellulose for alcohol determines the composition of the solvent mixture which gives the solution a minimum viscosity, a variation of concentration of nitrocellulose, in that it would alter the quantity of alcohol required to "saturate" the nitrocellulose in the system, should result in an alteration of the amount of alcohol necessary for the solution with a minimum viscosity. But it was shown that the solvent required to give this solution was independent of the concentration. Since it is necessary to introduce this property of nitrocellulose (*i.e.*, the alcohol affinity), it is difficult to see how the "complex theory" can explain this experimentally established fact.

Still another objection can be raised on the matter of influence of water. One would expect that mixtures of dry ether and dry alcohol should contain more of this ether-alcohol complex than if water were present in addition. Dry ether-alcohol mixtures should therefore give nitrocellulose solutions of lower viscosity than mixtures containing water. This is not realised in practice. On the contrary, the former solutions are stiff jellies, while under corresponding conditions the latter are fluids. We thus see that, in the light of this somewhat quantitative investigation, this theory appears to be very improbable.

Dr. Irvine Masson: The first effect of "solvents" on nitrocellulose is that they are taken up in some manner and are dissolved uniformly in the substance of the nitrocellulose; and we have to remember that whether a liquid is a so-called gelatinizing solvent or not, depends on one thing that has not been mentioned, and that is temperature. If you take nitrocellulose and moisten it with alcohol, nothing happens; but if you cool this mixture with solid CO_2 at a temperature of 80° , the alcohol is quickly absorbed by and gelatinizes the fibres. With ether containing no alcohol, under similar conditions, you do not get any gelatinization at temperatures attainable with liquid air. Such effects as these, and incidentally the fact that aqueous alcohol at low temperature is a still better gelatinizer than is absolute alcohol, must be borne in mind in considering any general theory of gelatinization.

In connection with the existence of an optimum mixture of binary liquids which gives the minimum viscosity when nitrocellulose is dispersed in it, in the case of ether-alcohol the optimum percentage is somewhere in the neighbourhood of 50 molecules of alcohol and 50 molecules of ether on the average. This would naturally suggest that an equimolecular complex of ether and alcohol is the chief agent in gelatinizing and dispersing; but, while this may be true, there are one or two points which must be borne in mind in making such an inference. We are at a loss to know what is the real composition of the liquid after the nitrocellulose has dispersed itself in it. We do not know how much solvent as a whole has been absorbed by the nitrocellulose to form the gel which has been dispersed, nor do we know the ratio of ether to alcohol in the gel particles. There is undoubtedly a selective absorption by the nitrocellulose, which leaves the composition of the residual fluid at equilibrium different from the original synthetic composition of the solvent. For that reason we must be careful in making deductions from experimental data in which we find a minimum viscosity with a particular *initial* percentage of ether in the alcohol, the percentage being taken before admixture with the nitrocellulose. It is rather difficult to arrive at

an idea of the amount of liquid which can be so taken up by the nitro-cellulose, but one can get an approximation to it by putting nitrocellulose fibrous pulp in vessels kept saturated with the vapour of different mixtures of the two liquids in question. If one does that with these mixtures, it is found that there is a particular mixture from whose vapour the nitrocellulose absorbs far more total weight of material than at any other. There is an optimum mixture, in fact, at which absorption is at its greatest value. It may be nothing more than a coincidence, but it is a fact that that optimum composition is very near to the 50:50 molecular ratio which we meet with in studying ether-alcohol viscosity systems. In the matter of complex formation, I think we may defer for the moment to the physicists, who argue on thermodynamic grounds and have shown, as Prof. Porter has shown recently, that from the vapour pressure curves of binary liquids one may not with security deduce the existence of chemical compounds. One may deduce what may be called a mutual interaction between the two liquids concerned, and if we rest content with that, I think that is as far as we are entitled to go for the present. There is undoubtedly some interaction in the particular case of ether and alcohol, and without doubt that interaction favours the absorption of these liquids by nitrocellulose and, as a consequence, the degree to which the nitrocellulose is dispersed; the viscosity and all other physical properties are correspondingly affected.

Mr. F. Sproxton said that the views expressed by Sir R. Robertson on the relation between viscosity and toughness were the opposite of those held in the celluloid industry. The divergence of opinion might be due to the difference in the nitrogen percentage of the nitrocellulose employed, and the presence of camphor in celluloid might affect the question. He thought it more likely, however, that cordite and celluloid received such different handling that a test which would be adequate for one would not be so for the other. Presumably the bending test which Sir R. Robertson described, measured the tensile strength of the outer skin of the cordite. In the celluloid industry little importance was attached to tensile tests. Many celluloid substitutes showed good tensile tests, but little elongation; such materials were brittle and would crack under shock—*e.g.*, if a sheet were brought down sharply on the flat surface of a table. Celluloid made from nitrocellulose of low viscosity was brittle when tested in the same way. The best test of the mechanical value of celluloid was to put a few hundredweights through the shops where articles were made, and note the fraction of material thrown out; but this could not be regarded as a satisfactory position from the scientific point of view.

Mr. F. Sproxton, replying to the discussion, regretted that in his endeavour to be brief, he had apparently given the impression that he unreservedly accepted Baker's theory. That was not the case. Baker's deductions were criticised by Bingham, and they were also rendered doubtful by Bramley's work on binary mixtures. Nevertheless, they had not been definitely disproved, and he had attempted to examine recent evidence using the theory as a basis for discussion.

Sir Robert Robertson : I think Mr. Sproxton might have claimed rather more than he did in his paper. He has brought out a matter of great importance in recalling the work of Will on the hygroscopicity

of nitrocellulose. Will found that the percentage of water taken up by a nitrocellulose together with the nitrogen percentage is a constant, thus showing the extent to which the unesterified hydroxyl groups are capable of taking up water. This seems to me to have a very important bearing on the question of the solubility of nitrocellulose in ether-alcohol solutions. In the first place, when the ether and the alcohol are both anhydrous, nitrocellulose goes into solution only with great difficulty and the viscosity of the solution is very high. Now, when a ternary diagram is constructed from the three constituents of the solution, ether, alcohol and water, we get a minimum viscosity when a considerable amount of water is present, about 8 per cent. with a nitrocellulose of 12.15 per cent. of nitrogen. Dr. Masson and others have found also that acetone in an anhydrous condition is a poor solvent for nitrocellulose, but that when 6 or 7 per cent. of water is present a minimum viscosity is obtained. Again, to-night Dr. Barr has shown us that with acetyl cellulose an acetone and water solution gives a definite minimum of viscosity, acetone-alcohol a much less definite one, and with acetone-benzene a straight line is obtained. It must also be borne in mind that the minimum viscosity of solutions of nitrocellulose, as described in the papers mentioned, was arrived at with ether-alcohol of which the alcohol had 8 per cent. of water. The subject wants following up something on the lines of McCall and Highfield, by working out further ternary diagrams with nitrocelluloses containing different contents of nitrogen. We may then get further information by considering these in conjunction with Mr. Sproxton's suggestion of the possible influence of the unesterified hydroxyl groups in the nitrocellulose. We may thus get nearer to explaining the mysterious question as to why nitrocellulose is dissolved by ether-alcohol, neither of which, by itself, will dissolve it.

The cords of nitrocellulose of high nitration were manufactured so as to be all of the same diameter, thus avoiding corrections on the application of the test for fragility on bending. When nitrocelluloses of different degrees of nitration are tested for viscosity in acetone, it is found that a striking fall in viscosity sets in about the region at which they would become soluble in ether-alcohol. Below this are the usual soluble nitrocelluloses, but the nitrocellulose used for the experiments described has a high degree of nitration and a very high viscosity. Attention was called to the effect produced as an example of the need for following up the investigation of the physical properties of solutions of increasing concentration right up to the solid product from which the solvent has been dried out, a subject which includes work on such substances as celluloid.

Mr. W. Harrison (*communicated*):

With regard to the observation of Duclaux and Wollman referred to in Mr. Sproxton's paper, that nitrocellulose solution can be separated into fractions giving widely different viscosities, it is interesting to note that starch solution can be separated by alcohol in a similar manner. In the case of starch, however, it has been found that the various fractions are apparently interconvertible. The most soluble fraction can be converted into a less soluble form by drying, and the least soluble form rendered more soluble by disintegration such as by the vigorous shaking of the solution.

Dr. G. Barr and Mr. L. L. Bircumshaw (*communicated*) :

The minima in the viscosity concentration curves for acetone water and acetone-alcohol are, perhaps, most simply explained on the assumption that the "best solvent" for cellulose acetate is the unimolecular form of acetone, and that the degree of dispersion is reduced by the presence of either associated acetone or of the diluent added. Acetone is usually supposed, mainly on the evidence of the variation of surface-tension with temperature, to consist largely of a trimolecular form. The addition to it of the strongly associated substances, water or alcohol, would rapidly increase the concentration of unimolecular acetone, water being more effective than alcohol, and so increase the solubility of the cellulose acetate: this solubility would eventually be reduced, and the viscosity increased, by the further addition of water or alcohol since the acetate is comparatively insoluble in these liquids. Benzene, being practically non-associated, would be less efficacious in increasing the proportion of unimolecular acetone, and since it has even less solvent action than alcohol, the absence of any fall in viscosity is readily understood on this view.

A study of the physical properties of binary mixtures of acetone with the three diluents used in the above investigation has revealed no evidence which would point to the production of a complexes such as that postulated by Baker for his ether-alcohol mixtures to explain the solubility of nitrocellulose. The only obvious maximum in the curves connecting density, surface-tension or viscosity with molar concentration, occurs at the water end of the viscosity concentration curve for acetone-water.

A similar hypothesis would appear to afford a simpler explanation of the variation of solubility and of viscosity of the solutions of nitrocellulose in ether-alcohol with the composition of solvent mixture than was suggested by Baker. The "best solvent" for nitrocellulose would, on this view, be non-associated alcohol, the proportion of which would be increased by the admixture of ether. Since ether is very little associated a considerable volume must be added to give a large proportion of unimolecular alcohol. The effect of small quantities of water on the solubility in ether-alcohol is qualitatively predicable from the hypothesis. The variation of the composition of the optimum mixture with the hygroscopicity of the nitrocellulose to which Mr. Sproxton has referred, and of which he mentions an explanation based on the ether-alcohol-complex theory, is capable of a somewhat similar interpretation on the hypothesis that non-associated alcohol is the most active dispersion medium.

The suggestion which we have advanced in the hope of stimulating discussion and research on these interesting relationships has, it would appear to us, the following advantages over a theory involving the assumption of the formation of a complex :—

(1) It is in accord with the known effects of the dilution of an associated liquid by another of any degree of association, and does not require the postulation of a compound for the existence of which there is little or no evidence.

(2) The assumption that simple molecules possessing considerable "residual affinity," are more readily attached to the cellulose ester molecule, *i.e.*, are better solvents than are the associated forms seems more probable than the ascription of similar facility of attachment to a more saturated complex.

(3) It avoids the necessity of assuming the existence of a fresh complex for each diluent considered: the same hypothesis explains the increased solubility of nitrocellulose in mixtures of alcohol either with ether or with toluene, and of acetylcellulose in mixtures of acetone either with water or alcohol.

(4) The very large influence of temperature on the dispersion (as indicated by viscosity) of colloidal solutions such as these, is obvious on the theory which we propose, since rise in temperature rapidly increases the proportion of unimolecular solvent; on the complex theory the proportion of complex would have to decrease with rise in temperature unless it were endothermic.

Dr. H. P. Stevens : Mr. Porritt has described the changes taking place in rubber under two heads: the first in which the rubber becomes tacky, and the second in which it becomes brittle. I do not think a rubber necessarily goes through both these changes. I think he will agree with me that a raw rubber becomes tacky, whereas a vulcanized rubber becomes brittle. When vulcanized rubber goes brittle with age, the change is apparent owing to a gradual stiffening, and the rubber does not pass through any tacky stage. I think the author's discovery of the gel formation of a raw rubber sol in a sealed tube is a new and exceedingly interesting one.

(Communicated) :

Mr. Porritt states in his paper: "It is surprising that none of the published investigations dealing with the perishing of rubber contain any reference to the pungent acid odour which under ordinary conditions is a well-marked feature of the change" (perishing of rubber).

Mr. Porritt did not read his paper *in extenso* at the meeting and a printed proof was not available, otherwise I should have remarked on the above paragraph. I was, I believe, the first to examine the pungent acid odour to which Mr. Porritt refers, and the matter is dealt with in my paper on the "Nature of Vulcanisation" (*Jour. Soc. Chem. Ind.*, July, 1919, p. 196r) where I wrote as follows: "During ageing, vulcanised rubber emits a pungent odour and gives off acid vapours due to a trace of a volatile product containing sulphur. When passed into water, this substance is retained and the solution reduces ammoniacal silver nitrate."

As the perishing of rubber is a process of oxidation, it is curious that the vapour given off should have reducing properties.

Dr. E. H. Rayner : With regard to the effect of light on rubber, I should like to emphasize the importance of the effect of light on ebonite, which is a very serious matter. For many years we have been very much troubled with it. Ten years ago, at the National Physical Laboratory, we did a long research on all kinds of ebonite. One of the objects was to find an ebonite, if possible, that was not affected by light. Of 20 or 30 samples we obtained, we did not find a single one that did not act as a sulphuric acid manufacturing plant when exposed to daylight, especially in a damp atmosphere. These 30 samples have now been exposed to light for 10 years, and they still go on generating sulphuric acid. They get washed occasionally with alkali and soap, but they start again, and this morning I tried one by putting a penny on a piece of ebonite and connected it to a low-resistance portable galvanometer. A pen-knife was connected with the other terminal of the galvanometer, and quite an appreciable

deflection was produced. The insulation resistance was of the order of 1/20th megohm with two pennies half-an-inch apart. That being so, the leakage across the ebonite mounting of a standard resistance of the order of a megohm may be important with ebonite in a very much better condition than the sample mentioned. We have had to design resistances to avoid this trouble, but the production of an ebonite which is not affected by light is badly wanted in the electrical industry, especially where the laboratories have a top light and a damp atmosphere. If, therefore, somebody can suggest a method of making ebonite which is not so affected, we should be very grateful.

Prof. A. W. Porter : Even sulphur itself becomes conducting under the action of light, and perhaps the conducting power in ebonite is one that is simply inevitably associated with it, and you will never be able to get rid of it without getting rid of the sulphur. Sulphur behaves something like selenium, only to a smaller extent.

Mr. Rayner : Does sulphur form sulphuric acid in the air ?

Prof. Porter : I do not know what change occurs, but it becomes conducting.

Dr. Stevens : The moisture no doubt helps conductivity. The sulphuric acid is formed and absorbs moisture. You cannot have anything better than a damp atmosphere to prevent oxidation taking place.

Mr. B. D. Porritt : The serious deterioration in the insulating properties of ebonite resulting from exposure to light, to which Dr. Rayner has made reference, is almost certainly due to the formation of a film of sulphuric acid on the surface. This probably is to be attributed to the oxidation of free sulphur since the rubber sulphur compound which constitutes ebonite is a relatively stable compound.

In respect to Dr. Stevens's remarks on the subject of "tackiness," this is certainly a characteristic of raw rubber and is not manifest during the changes which take place during the oxidation of vulcanised material regarding which comparatively little is known.

SECTION V.—PRECIPITATION OF DISPERSE SYSTEMS

A communication by Dr. R. S. Willows opened the consideration of this section of the subject.

THEORY OF PRECIPITATION OF DISPERSE SYSTEMS

BY

R. S. WILLOWS, M.A., D.Sc., F.Inst.P.

The subject of colloids has hitherto attracted few English workers in physics in spite of the splendid field for research. One object of the discussion is educative: to show the extent and interest of this field. It was this aspect that was mainly kept in view in the preparation of this note.

Of nearly all the work on precipitation of sols or emulsions by added electrolyte the common criticism can be made that faulty methods are used for determining when the same definite stage in the precipitation has been reached. Thus the settlement of the precipitate in an arbitrarily chosen time or a fractional change in viscosity have been used to fix a measuring point, but their connection with the earliest stage of precipitation—the coalescence of pairs of colloid particles—is at best a distant one and is perhaps masked by other factors. Some work by Zsigmondy and his pupils on rapid coagulation appears to be quite definite in its results and has the further advantage for our present purpose, that the conditions chosen are such as to admit of its mathematical treatment.

Zsigmondy finds it is possible in the ultra-microscope to distinguish between the yellow-green primary and the secondary particles in a gold sol, the latter being formed by the coalescence of two primary particles. The method of experiment is as follows:—Having determined, by counts in an ultra-microscope, the number, N , of primary particles per unit volume of a red gold sol, electrolyte is added in a definite volume: when a certain easily recognised colour tint appears a solution of gum arabic is added, which by its protective action stops further coalescence. A recount is now made either of (a) the primary particles per unit volume, N_1 in number (Zsigmondy), or (b) the total number, ΣN , of particles, primary, secondary, &c. (Westgren and Reitstötter). These can be compared with the results calculated from Smoluchowski's theory, of which an outline is given below.

Earlier experiments on precipitation have shown a marked influence of the nature of the electrolyte, when the time of coagulation is an hour or longer, but these of Zsigmondy's, on rapid coagulation, show that for the gold sol used the time of coagulation cannot be reduced below five or six seconds with electrolyte concentration varying between fairly wide limits, and that this time is independent of the valency, &c., of the ions. Rapid coagulation is, in fact, conditioned entirely by rapidity of diffusion. By comparing the results obtained, when different amounts of electrolyte are added, with others of Galecki, in which the relative charges on the sol particles are measured, the conclusion

is reached that rapid coagulation occurs before the iso-electric point is reached. This agrees with Powis's results on emulsions; but whereas Powis found that it was sufficient to reduce the potential difference across the double layer from 0.04 to 0.03 volts in order to start coagulation, the discharge of the gold particles had to be much more complete.

In his theory of these experiments Smoluchowski assumes that the particles attract each other by "capillary" forces (nature not specified) when they approach each other, but that normally coalescence is prevented by the double electric layer which must first be broken. When electrolytes are added this layer is wholly or partially destroyed by ionic adsorption (mechanism not specified). Brownian motion tends to bring the particles into contact, and he further assumes that whenever the distance between two centres becomes less than R' that coalescence occurs.

By a beautiful piece of mathematical work the author calculates the number of primary particles N_1 , the secondary particles N_2 , &c., and the total number of particles of all classes, ΣN , present in unit volume at a time t after the addition of electrolyte. To save space, only Zsigmondy's results are dealt with here. The equation from which to calculate N is:—

$$4\pi DRN = \frac{1}{t} \left[\sqrt{\frac{N}{N_1}} - 1 \right].$$

where Einstein's diffusion constant $D = \frac{R\theta}{n} \cdot \frac{1}{6\pi\mu r}$

R = gas constant.

n = Avogadro's number.

μ = viscosity of medium at abs. temp. θ .

r = radius of particles.

Some of the results are given in the table.

$t(\text{secs})$	N_1 obs.	N_1 calc.
2	1.42	1.71
10	1.17	1.14
20	.75	.76
30	.52	.53

It should be noticed that Smoluchowski's work is entirely statistical; he does not attempt to account either for the double layer, the adsorption of the electrolytic ions or for the assumed attraction between the sol particles. A complete theory must explain the origin of the charge on the particles and how the discharging ions penetrate the double layer against the repulsion of the external half.

Two points appear to be fairly established. The stability, at least of emulsions, depends only on the potential difference across the double layer, as shown by Powis; and, contrary to Bredig's theory, Ellis finds no relation between surface tension and the coagulation of emulsions.

THE ORIGIN OF THE CHARGE OF A COLLOIDAL PARTICLE AND ITS NEUTRALISATION BY ELECTROLYTES

BY

JNANENDRA NATH MUKHERJEE

The origin of the charge of a colloidal particle is generally referred to the adsorption of ions. Regarding the mechanism of the adsorption we have no definite idea. In his theory of adsorption Langmuir* refers it to "chemical forces" due to the surface atoms. The adsorption of an ion gives a charge to the surface, and as a result introduces electrical forces. The recognition of this factor elucidates the influence of electrolytes on the precipitation of suspensoids on electro-osmosis and allied phenomena.

THE CHARGE OF SUSPENSIDS

It is well known that the stability and the charge of suspensoids are connected with traces of electrolytes. Table 1 shows that for most suspensoids *the charge is of the same sign* as that of the "ion" the substance has in common with the peptising or stabilising electrolyte. Most suspensoids (excepting colloidal metals and other elements) are included in the table.

TABLE 1

Suspensoid.	Stabilising Electrolyte.	Common Ion.	Sign of the Charge of the Particles.
¹ Insoluble silver salts -	(a) Silver nitrate - (b) Electrolyte with common anion.	Ag ⁺ - Anion -	Positive. Negative.
² Metal sulphides	Hydrogen sulphide or ammonium sulphide.	S ²⁻ or HS ⁻ -	Negative.
³ Ferrocyanides of copper, and iron.	Potassium ferrocyanide	Anion -	Negative
⁴ Hydroxides of iron, aluminium, etc.	Nitrate or chloride of the corresponding metal.	Cation	Positive.
⁵ Hydroxide of iron -	Alkali hydroxide	Hydroxidion -	Negative.
⁶ Barium carbonate -	Barium nitrate -	Barion -	Positive.

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 - ³ Duclaux, *Compt. Rend.*, 1904, **138**, 144, 571; *J. Chim. Phys.*, 1909, (vii), 405.
 - ⁴ Pauli and Matula, *Koll. Zeitsch.* 1917, **21**, 49; Duclaux, *J. Chim. Phys.*, 1907, **5**, 29.
 - ⁵ Powis, T., 1915, **107**, 818.
 - ⁶ Perrin, *J. Chim. Phys.*, **2**, 1904, 601.
- Compare also for "stannic hydroxide" Biltz, *Ber.*, 1904, **37**, 1095 and Glixelli, *Koll. Zeitsch.*, 1913, **13**, 194.

The relationship shown in Table 1 makes it possible to define the chemical forces involved in this particular case. The fixation of a common ion is due to the same causes that bring about the growth of a crystal in its solution.

* *J. Amer. Chem. Soc.*, 1916, **38**, 2221; *ibid.*, 1917, **39**, 1848.

The growth of a crystal in its solution shows that the surface atoms of a solid attract the molecules of which it is composed, and that the "atoms" or "groups" in the molecule are attracted most strongly at specific points in the surface. The "attached" molecule thus conforms to the structure of the crystal. As an example one may say that at the surface of a crystal of sodium chloride there are "places" where the chlorine ion in salt solution can be held by chemical forces. The specific nature of chemical forces requires that the same attraction will be present when the crystal is in contact with any other solution of an electrolyte, which gives a "chlorine ion" in an aqueous solution. Thus on the addition of hydrochloric acid the chloridions will be attracted. If "N" be the number of "places" per unit surface where the chloridions are attracted chemically, then the number remaining "attached" to the surface (at any instant) will be dependent:—

(1) On the concentration of the "ion," and

(2) "A" the work necessary to separate the "ion" from its position in the surface. "A" is evidently the measure of the chemical affinity acting on the "ion," and $e^{-A/kT}$ is a measure of the stability of the "fixation" where $k = \frac{R}{N_0}$, R being the gas constant, N_0 the Avogadro number, and "T" is the absolute temperature. For a stable union it is necessary that "A" should be great compared to kT . In this case a small amount of an electrolyte with an adsorbable "ion" will be sufficient to lead to the adsorption of an appreciable amount of the "ion." Since the molecules of sodium chloride and hydrochloric acid do not combine with each other in their entirety this sort of "fixation" of the chloridion will impart a charge to the surface.

The resulting separation of electricity will be opposed by the electrical attraction exerted by the cations in the surrounding liquid.

THE ELECTRICAL ATTRACTION ON IONS OF OPPOSITE CHARGE

We shall speak of the "ions" fixed to the surface by chemical forces as "chemically adsorbed." *In the following discussions it is assumed that there is no chemical affinity acting between "ions" of opposite charge.* This assumption is obviously made to investigate the effect of the electric forces alone.

In consequence of the charge, ions of opposite sign will be drawn near the surface. In the liquid there remains an equivalent amount of ions of opposite sign. The electrical energy will be minimum when these ions are held near the surface so that the distance between the oppositely charged ions has the minimum value possible under the conditions, and they will be held opposite to the ions chemically adsorbed. An "ion" so held will not be "free" to move if its kinetic energy is less than "W", the energy required to separate the ion from the oppositely charged surface.

The number of such "bound" ions determine the diminution in the charge of the surface. When the concentration of ions of opposite charge in the liquid is small the number of ions "held" to the surface by electrical attraction will be small. The equilibrium conditions will be discussed more fully later.

If the chemically adsorbed ions have a valency equal to " n_1 " and " n_2 " is the valency of the oppositely charged ions in the liquid in contact with the surface then

$$W = \frac{n_1 n_2 E^2}{D x} \quad \dots \quad (1)$$

where E = the electronic charge, x = the distance between the centres of the "ions" at the position of minimum distance, and " D " is the dielectric constant of water. Since "ions" have probably an envelope of water " x " has a value of the order of 10^{-7} cm (the diameter of the molecules of water is about 4×10^{-8} cm.). The probability of an ion remaining fixed is given by $1 - e^{-W/kT}$ where " k " and " T " have the same significance as before. The values of $1 - e^{-W/kT}$ for different values of n_1 and n_2 are given below.

TABLE 2.

$x = 10^{-7}$ cm. $D = 81$. Values of $1 - e^{-W/kT}$

$T = 27^\circ\text{C} \cdot k = 1.37 \times 10^{-16}$

$E = 4.77 \times 10^{-10}$ C.G. S units.

	$n_2 = 1$	$n_2 = 2$	$n_2 = 3$	$n_2 = 4$
$n_1 = 1$.501	.751	.875	.938
$n_1 = 2$.751	.938	.984	.986
$n_1 = 3$.875	.984	.998	X

Since the value of " x " is not known definitely, Table 2 conveys a rough idea of the order of magnitude of $1 - e^{-W/kT}$

A consideration of the values given above will show that the electrical attraction is sufficiently strong to account for the adsorption.

THE DOUBLE LAYER

Depending on the concentration of the oppositely charged ions in the liquid near the surface at any instant a certain number of the "chemically adsorbed" ions are "covered" by "ions" of opposite charge. In the liquid near the surface there are always a number of free "ions" equivalent in amount to the "uncovered" chemically adsorbed ions on the surface. The total amount of ions of opposite sign both "bound" and "free" is equivalent to the amount of ions "chemically adsorbed." These "free" ions form the second sheet of the double layer. It is evident that as a result of their thermal motion the mean distance between the two layers will be greater than " x ."

CONDITIONS WHEN EQUATION 1 HOLDS GOOD

" W ." has the value given in Equation 1 when the mean distance between the chemically adsorbed ions is considerably great compared to " x ," i.e., molecular dimensions. The two oppositely charged ions can then be assumed to be uninfluenced by neighbouring ions on the surface. The considerations set forth below show that for practical purposes we can treat the charge of the surface as due to discrete charged particles widely separated from each other compared to molecular dimensions.

Following Helmholtz and Lamb (*Brit.-Assoc. Rep.*, 1887, p. 495; *Phil. Mag.*, 1888, p. 60) it is usual to consider the thickness of the double layer to be of the order of molecular diameters. McTaggart (*Phil. Mag.*, 1914, [6], 27, 297) calculates the "density" of the charge at the surface of gas bubbles to be 1.5×10^4 C.G.S. units (from the well-known Lamb-Helmholtz equations). He assumes that a layer of water of thickness of about 10^{-8} cm. separates the opposite charges. Since the electronic charge is 4.77×10^{-10} C.G.S. units (Millikan's value) the number of univalent "ions" which must be adsorbed per unit surface (cm^2) is equal to about 10^{13} . The mean distance between the "ions" will be about 3×10^{-6} cm. The

distance is greater if the charge is due to adsorbed polyvalent "ions." For a thickness of the double layer of the order of 10^{-6} cm. the mean distance is 3×10^{-5} cms. Similar values of the "density" of the charge are obtained from other data (cp. Lewis, *System of Physical Chemistry*, 1916, Vol. 1, p. 407). Thus we find that the "ions" imparting the charge to the surface are situated wide apart compared to molecular dimensions. Under these conditions the neighbouring ions have comparatively little effect on an oppositely charged "ion" at its position of minimum electrical energy and "W" as given in Equation 1 can for practical purposes be taken to be the measure of the stability of the electrical adsorption of ions of opposite charge.

THE MAXIMUM ELECTRICAL ADSORPTION ON THE ADDITION OF AN ELECTROLYTE

It will appear from Table 3 that the addition of an electrolyte with univalent "ions" of opposite sign to the charged surface seldom produces a reversal in the original charge. If, however, the electrolyte has a bivalent ion of opposite sign reversals are sometimes observed. On the other hand, with electrolytes having multivalent ions of opposite sign a reversal of the charge is more frequent.

TABLE 3

Substance.	Sign of Charge.	Electrolytes.	
		No Reversal.	Reversal.
¹ CrCl ₂	Made "positive" by the addition of acid.	Ca(NO ₃) ₂ - - MgCl ₂ - -	K ₃ Fe(CN) ₆ . K ₄ Fe(CN) ₆
² CrCl ₃	Made negative by the addition of alkali.	MgCl ₂	Ba(NO ₃) ₂ , Ca(NO ₃) ₂
³ Al ₂ O ₃ -	"Positive" with acid.	MgSO ₄ - Ca(NO ₃) ₂ - -	K ₄ Fe(CN) ₆ .
⁴ Al ₂ O ₃ -	"Negative" with	x	Ca(NO ₃) ₂ .
⁵ Mn ₂ O ₃	"Negative" with base.	x	Ba(NO ₃) ₂ .
⁶ Carborundum.	"Negative" with base.	x	La(NO ₃) ₃ .
⁷ Glass -	Negative	K ₂ SO ₄ , KNO ₃ , NaCl	Thorium nitrate.
⁸ Quartz }		HNO ₃ , Ce(NO ₃) ₃ , UO ₂ , (NO ₃) ₂ , AgNO ₃ , Al ₂ (SO ₄) ₃ , BaCl ₂ , CaCl ₂ .	Thorium nitrate.
⁹ Copper hydroxide.		KCl, K ₂ SO ₄ , Al ₂ (SO ₄) ₃	K ₃ PO ₄ , K ₃ Fe(CN) ₆ .
¹⁰ Gas bubbles	Negative	HCl, HNO ₃	La(NO ₃) ₃ , Th(NO ₃) ₄ , Zr(NO ₃) ₄ , Al ₂ (SO ₄) ₃ , Al ₂ (SO ₄) ₃ .
¹¹ Silver, gold	Negative - -	KCl, BaCl ₂ , Al ₂ (SO ₄) ₃ KCl. - -	Th(NO ₃) ₄ .
¹² As ₂ S ₃ -	Negative		BaCl ₂ , Al ₂ (SO ₄) ₃ , Th(NO ₃) ₄ .
¹³ Emulsions	Negative		K ₃ Fe(CN) ₆ , K ₄ Fe(CN) ₆ .
¹⁴ Gas bubbles	"Positive" with thorium nitrate.	x	

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- ^{9, 11} Burton, *Physical Properties of Colloidal Solutions*, 1916, 151, 153.
- ^{10, 14} McTaggart, *Phil. Mag.*, 1914(6), **27**, 297, 12; Powis, T., 1916, **109**, 734.
- ¹³ Powis, *Zeitsch. Physikal. Chem.*, 1914, **89**, 91, 186; also T., 1915, **107**, 818.

It is difficult to reconcile these facts with the specific nature of the "adsorption" of ions. They are, however, a necessary consequence of the view advanced here. Let us suppose that the "primary ions" which are chemically adsorbed are all univalent. An ion of opposite sign entering the "double layer" will be driven towards the surface by the strong electric field. An "ion" of the same sign will rarely strike the surface. The oppositely charged ions will be held to the surface by electrical forces near each primary ion. The maximum number of ions which can possibly be held in this manner per unit surface is equal to the number of primary ions in the same area. If the oppositely charged ions are univalent it is evident that when the maximum adsorption has been reached the surface is neutral. In general when the primary ions are univalent the maximum possible charge per unit surface is equal to—

$$NE(1 - n_2) \dots \dots \dots (2)$$

where "N" is the number of univalent "primary" ions per unit area, E, the electronic charge and "n" the valency of the oppositely charged ions.

For the general case the possible maximum charge is given as

$$NE(n_1 - n_2) \dots \dots \dots (3)$$

where "n₁" is the valency of the "ions" chemically adsorbed and N, E and n₂ have the same significance as before.

Thus a reversal of charge by "electric adsorption" is theoretically possible only when the added electrolyte has an oppositely charged ion with a valency greater than the primary ions. For univalent "ions" of opposite sign reversal is impossible by electrical adsorption. In considering particular cases it should be remembered that "chemical action" is quite possible. It is satisfactory to note that in Table 3 there is not a single case of reversal with univalent ions of opposite sign.

Actually, however, the maximum adsorption will coincide with the neutralisation of the surface. The collisions of "ions" of opposite sign are mostly due to the electrical field of the double layer, and the collisions due to "diffusion" are comparatively negligible. The number of collisions will diminish rapidly with increased electric adsorption, and will have a small value at the neutral point. Farther adsorption will impart to the surface a charge of the same sign as the "ion" and the double layer will now repel the "ion" from the surface. The number of collisions will decrease rapidly and will soon be negligible. Thus a reversal of charge is only possible when the valency of the oppositely charged ion is very great, so that $1 - e^{-W/kT}$ has a considerable value. Even then the theoretical maximum adsorption is not possible, and the reversal in charge can proceed only to a small extent. In the majority of cases, therefore, the maximum adsorption will correspond to a neutralisation, or reversal to a slight extent.

EQUILIBRIUM CONDITIONS

In discussing the equilibrium conditions we shall deal with the case when the maximum adsorption corresponds to the neutralisation of the charge. The "maximum" amount of an ion of opposite sign that can be adsorbed per unit area is thus equivalent to the charge per unit area. If the charge of the surface is due to "N" ions of valency n₁ per unit area, then the maximum number N of an

"ion" of valency " n_2 " and of opposite signs which can be adsorbed electrically is given by the relation

$$N_m = N.n_1/n_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)^*$$

Let " θ_1 " denote the fraction of this maximum which has been adsorbed when equilibrium has been reached in presence of ions of opposite sign having a concentration " c " in the liquid. For equilibrium the number of electrically adsorbed ions becoming "free" in any interval per unit area must be equal to the number re-adsorbed in the same time.

Considering unit surface the rate at which the adsorbed ions of opposite charge become "free" is evidently given by

$$k_1.N_m.\theta_1.e^{-W/kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

since $N_m\theta$ is the number of "ions" adsorbed per unit surface k_1 is a constant.

The rate of adsorption depends on two factors: (a) the rate of collision of oppositely charged ions, and (b) the number of "places" where adsorption is possible; that is, the number of primary "ions" that remain "uncovered" and unneutralised by oppositely charged ions at any moment. (Cf. Langmuir.) This is given by

$$N - N_m\theta_1 = N(1 - \frac{n_1}{n_2} \theta_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The rate of collisions (a) is determined by the concentration of ions of opposite sign in the liquid in contact with the surface and the forces driving the ions towards the surface. Each "ion" is urged to the surface by two forces:—

(1) *Its thermal agitation to which its osmotic pressure is due.*—

According to Einstein this force is equal to $\frac{RT}{N_0}$.

(2) *The electrical attraction exerted on the particles by the charged surface.*—An ion in the double layer is acted on by its electrical field. The intensity of the field is proportional to the "density" of the charge on the surface, and is, therefore, given by:

$$k'_2(1 - \theta_1)n_1N.n_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7).$$

Since " n_1 " and " N " are constants for the same surface we may write (7) as—

$$k_2(1 - \theta_1)n_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a) \text{ where } k_2 \text{ is a constant.}$$

The thickness of the surface layer is small and the rate of fall in the potential, that is, the intensity of the electric field, is enormous. A simple calculation will show that RT/N_0 is negligible in comparison to $k_2(1 - \theta_1)$. Under the conditions the rate of collision is given by—

$$k_3n_2(1 - \theta_1).C.u \quad . \quad . \quad . \quad . \quad . \quad . \quad (8),$$

where " C " is the concentration of the "ions" in the liquid in contact with the surface, " u " is the "mobility" of the "ion" (under unit force), k_3 is a constant, and " n_2 " and " θ_1 " have the same significance as before.

* Equation "4" holds when n_2 is equal to or greater than n_1 . When $n_1 > n_2$ more than one "ion" of opposite charge should be adsorbed for each chemically absorbed "ion" to neutralise its charge. The mutual repulsion of these "ions" brings in complications which will not be considered in the present paper.

From (6) and (8) we find that the rate of adsorption is given by—

$$k_4 \cdot N(1 - \frac{n_1}{n_2} \theta_1) \cdot n_2(1 - \theta_1) C.u. \quad (9).$$

Finally, for equilibrium we get

$$k_1 N_m \theta_1 e^{-W/kT} = k_4 N(1 - \frac{n_1}{n_2} \theta_1) n_2(1 - \theta_1) C.u. \quad (10).$$

Putting $N = \frac{N}{n_2} \frac{n_1}{n_2}$ and remembering that N_1 , n_2 , u and $e^{-W/kT}$ are constants for the same ion we can write equation (10) in the form

$$\theta_1 = k_0 \frac{n_2}{n_1} C.(1 - \frac{n_1}{n_2} \theta_1)(1 - \theta_1) \quad (11)$$

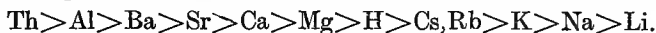
where $k_0 = \frac{k_4}{k_1} n_2 \cdot u \cdot e^{-W/kT}$.

[It may be stated that k_4 contains the term " $n_1 N$ " (cf. equation 7).]

Since " θ_1 " denotes the "fraction" of the original charge neutralised by adsorption the charge of the surface is proportional to

$$1 - \theta_1 = \theta_2 \quad (12).$$

Equations (1) and (10) show that the "electrical" adsorbability of an "ion" of opposite charge is dependent on its mobility and its valency. Thus for a "negative" surface the order of adsorption of the following cations should be



(Rubidium and Caesium have practically the same ionic mobility.)

It should be remembered that all along we have assumed that the surface does not exert any chemical affinity on the "ions." Clearly this is not likely to be the case always, and the order given above cannot be expected to hold good in such instances. The following section will show, however, that the above order holds good in a large number of cases.

THE PRECIPITATION OF A SUSPENSOID BY AN ELECTROLYTE

It was first pointed out by Hardy that the precipitation of suspensoids by inorganic electrolytes is due to a diminution in the electric charge of the particles. The "ion" having a charge of the same sign on the colloid has very little influence on the precipitation and the precipitating power of an electrolyte is determined by the "valency" of the "ion" which has a charge opposite in sign to that of the colloid. The same results have been observed in experiments on cataphoresis and electro endosmosis (cp. the works of Perrin, Burton, Elissafoff, McTaggart, Ellis, Powis, &c.). These regularities are not consistent with the specific nature of the adsorption process as it is ordinarily understood, and they show that the process of "adsorption" in these cases is "electrical" in nature.

Whetham (*Phil. Mag.*, 1899, **48**, 474) recognised the electrical nature of the process, and considering the probabilities of a charged particle meeting an equivalent amount of electrical charge of opposite sign in the form of ions deduced his interesting relation between the precipitating powers of "ions" of different valency.

In the application of his equation of adsorption isotherm to this process Freundlich (*Zeitsch. Physikal. Chem.*, 1910, **73**, 404) assumed that different ions are equally adsorbed at equal concentrations, the constants in the equation being independent of the nature of the "ion."

Subsequent work has shown that the simple relations indicated by these equations (of Whetham and of Freundlich) do not agree with observations. These theories do not attempt to elucidate the difference in the precipitating powers of "ions" having the same valency. Bancroft (*J. Phys. Chem.*, 1915, **19**, 363; *Rep. Brit. Assoc.*, 1918, Section B., pp. 2-16) and Wo. Ostwald (*Koll. Zeitsch.*, 1920, **26**, 28, 69) have admirably summarised the present position of the subject.

It is necessary to point out in this connection that the precipitation of a suspensoid by electrolytes is a complicated process. The diminution in the electric charge is undoubtedly responsible for the coagulation, but the precipitating concentration of an electrolyte is dependent on such other factors as the distance between the particles, their size, the total amount of colloid-liquid interface and "age." Ions of different valency (and hence different coagulating powers) are not all similarly affected by variations in these conditions. A diluted sol of arsenious sulphide requires a higher concentration of potassium chloride but a lower concentration of barium chloride than what the original sol requires. The ratio of the precipitating concentration of two electrolytes is thus variable (Mukherjee and Sen, T., 1919, **115**, 462; Mukherjee, T., 1920, **117**, 350; Kruyt and Duin, *Koll. Chem. Beihefte*, 1914, **5**, 269; Kruyt and Spek (*Proc. K. Akad. Wetenschap.*, Amsterdam, 1915, **17**, 1158). It is therefore clear that the precipitating concentrations (i.e., the precipitating powers) of an electrolyte cannot be taken as a *quantitative* measure of the adsorption of the "ions." The discussion of such data from a quantitative point of view of adsorption is thus not possible. As a result no direct quantitative relationship is possible between the diminution in the electric charge of a colloidal particle and the coagulating concentration. The precipitating powers of different ions thus give a qualitative measure of their adsorbability.

It will be seen from Table 4 that the order of the precipitating power of cation (on "negative" suspensoids) is as follows:—

Th>Al>Ba>Sr>Ca>Mg>H>Cs,Rb>K>Na>Li
the same as deduced from equation (10).

TABLE 4

Order of Precipitating Power of Cations for various Suspensoid Systems

1. Arsenious sulphide under different conditions.	Th>Al>Ba>Sr>Ca>Mg>H>K>Na>Li.
2. Gold - -	Al>Sr>Ca>Mg>H>Cs>Rb>K>Na>Li
3. Platinum - -	Al>Ba>K>Na.
4. Copper ferrocyanide	Al>Ba>H>Cs>Rb>K>Na>Li.
5. Prussian blue - -	Al>Ba>H>Cs>Rb>K>Na>Li.
6. Silver - - -	Al>Ba>Sr>Ca>H>Cs>Rb>K>Na>Li.
7. "Oil" emulsions -	Al>Ba>Sr>Ca>Mg>K>Na>Li.

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- Freundlich, *Zeitsch. Physikal. Chem.*, 1903, **44**, 129; Mukherjee, *J. Amer. Chem. Soc.*, 1915, **37**, 2024; *loc. cit.* Other "sulphides" behave similarly.
Galecki, *Zeitsch. Anorg. Chem.*, 1912, **45**, 221; Westgren, *Arkiv Kem. Min. Geol.*, 1918, **7**, No. 6, 1-30.
Freundlich, *Kapillarchemie*, 1909, 352; 4, 5; Pappada, *Koll. Zeitsch.*, 1910, **6**, 83, 1911, **9**, 136, 6; Pappada, *Gaz. Chim.*, 1912, **42**, I, 263.

7. The series given refer to both the order of the de-emulsifying power and the effect on the inversion of phase (privately communicated by Mr. S. S. Bhatnagar, *see also* T., 1920, 117, 542. *Also* Bach (*J. Chim. Phys.*, 1920, 16, 46) finds the series



for a number of cases).

It should be noted that in the experiments referred to in Table 4 inorganic "ions" only have been used, and that these cations have very little tendency to complex formation. The "alkali" metal cations have the least tendency for complex formation, and it is to be expected that they are most likely to be least affected by chemical affinity due to the surface atoms, and hence the "adsorption" should be mainly "electrical" in nature. The order of alkali cations as deduced from equation (10) determines the order of their precipitating powers in most cases. Pappada* first pointed out that the order of coagulating power of these ions is the same as the order of the mobility.

The Effect of Electrolytes on Electro-Endosmosis

A verification of equation (10) is possible from the experimental work on electro-endosmosis. Unfortunately the experimental difficulties are considerable and the limits of error quite great. The most careful work is that of Elissafoff (*Zeitsch. Physikal Chem.*, 1912, 79, 385) who considers the limits of error to be about 10 per cent. in his experiments. It will be seen from the following tables that the agreement is as good as can be expected.

In applying equation (10) or (11) it should be remembered that :

(a) Chemical action between the surface and the oppositely charged ion is not always negligible, and

(b) That the surface concentration is not always the same as that in the bulk of the liquid. Thus "adsorption" due to variation in surface energy in the sense of Gibbs' well-known equation is always possible.

The solid substances examined by Elissafoff are glass and quartz. We shall assume that the charge of the surface is due to the fixation of "hydroxyl ions" by chemical affinity.

From equations (11) and (12) we get

$$1 - \theta_2 = k_0 c \cdot \frac{n_2 - n_1}{n_1} \theta_2 + k_0 c \cdot \theta_2^2 \dots \dots \dots (13)$$

For hydroxyl ions $n_1 = 1$ and putting n_2 equal to 1, 2, 3, 4 successively we get the following equations for the adsorption of oppositely charged ions of valency 1, 2, 3 and 4 respectively.

$$k_0 c \theta_2^2 + \theta_2 - 1 = 0 \dots \dots \dots (13A).$$

$$k_0 c \theta_2^2 + \theta_2 (k_0 c + 1) - 1 = 0 \dots \dots \dots (13B).$$

$$k_0 c \theta_2^2 + \theta_2 (2k_0 c + 1) - 1 = 0 \dots \dots \dots (13C).$$

$$k_0 c \theta_2^2 + \theta_2 (3k_0 c + 1) - 1 = 0 \dots \dots \dots (13D).$$

There is only one unknown constant in these equations. For comparison the values of θ_2 calculated by Elissafoff from an empirical equation is also given. The unit of concentration is taken to be 10^{-6} gram-ion per litre.

* *Kolloid. Zeitsch.*, 1909, 4, 56.

TABLE 5

Electrolyte—sodium chloride $k_0 = \cdot 0076$.

Glass capillary concentration.	50 θ_2 obs.	50 θ_2 (Eqn. 13A).	50 θ_2 (Empirical equation).
22·5	43	43·4	42
68	37	36·4	34
136	31	30·6	29
225	26	26·4	26
2240	8	10·6	10
4500	5	7·8	5

TABLE 6

*Glass*Electrolyte—potassium sulphate $k_0 = \cdot 00875$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13A).	50 θ_2 (Empirical equation).
22	41	42·8	38
67	36	35·2	32
134	27	29·5	29
224	26	25·2	26
470	23	19·4	22
800	21	15·7	19
4000	8	7·7	10
7900	5	5·6	7

TABLE 7

*Glass*Electrolyte—silver nitrate $k_0 = \cdot 059$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13A).	50 θ_2 (Empirical equation).
4	42	41·2	39
7	35	37·3	35
10	32	34·5	34
20	29	28·6	30
50	27	21	25
1000	9	5·8	8

TABLE 8

*Glass*Electrolyte—barium chloride $k_0 = \cdot 0163$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13B).	50 θ_2 (Empirical equation).
2·2	47	46·7	—
4·4	46	44	—
6	41	42	39
22	28	31·5	30
110	15	15	20

TABLE 9

*Glass*Electrolyte—uranyl nitrate $k_0 = .0168$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13B).	50 θ_2 (Empirical equation).
3.5	52	—	—
7	45 (38)	41.1	39
10.5	38	38	36
14	36 (32)	35.4	33
28	29	28.5	27
56	23	21.3	21
112	14	14.5	15
140	13	12.6	13
238	5	8.7	9

The results of a second determination are given in brackets. For a concentration of 3.5 instead of a decrease a rise had been observed. These and other instances illustrate that the limits of error are considerable.

TABLE 10

*Glass*Electrolyte—nitric acid $k_0 = .059$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13A).	50 θ_2 (Empirical equation).
8	45	36.1	—
20	29	29.6	30
34	26	25	26
60	21	20.4	20
100	16	16.9	16

TABLE 11

*Quartz*Electrolyte—potassium nitrate $k_0 = .01$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13A).	50 θ_2 (Empirical equation).
8	48	46.6	—
28	43	40.6	43
68	33	34	33
120	28	29	26
390 (?)	10	19	13

TABLE 12

Electrolyte—calcium chloride $k_0 = .043$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13B).	50 θ_2 (Empirical equation).
1.6	43	44.4	44
4.3 (?)	28	37.7	36
8.1	32	31.9	31
13.5	28	26.5	27
29.5	20	18.3	21
82 (?)	19	9.6	12

Aluminium and thorium salts are hydrolysed to a large extent in such low concentrations as have been used by Elissafoff. The "hydroxide" has a positive charge in the colloidal state. Positively charged colloids can neutralise the charge of negatively charged colloids and equation (13) can no longer be applied.

From Table 7 we find that "silver nitrate" has a greater neutralising power than other monovalent ions. This should be attributed to chemical forces. Equation 13 holds good for the limiting case when there is no chemical attraction. In case of chemical action "W" as given in equation (1) no longer represents the stability of the adsorption of the ion. We can, however, put the energy required to separate the ion from the surface as equal to " $W + B$," where " B " is a measure of the chemical affinity acting on an ion. The form of the equation thus remains the same as in (13).

TABLE 13

	Ions.							
	Na ⁺	K ⁺	Ag ⁺	H ⁺	Ca ⁺⁺	Ba ⁺⁺	UO ₂ ⁺⁺	Surface
$k_0 \times 10^2$	76	87	5.9	5.9	x	1.63	1.68	Glass.
(Eqn. 13).	—	1.0	—	—	4.3	—	—	Quartz.

A discussion on the values of k given above is not possible unless we know " x " in Equation (1). If " x " has such a value that $-W/kT$ for a univalent ion is less than 0.2, then $e^{-W/kT}$ for a divalent ion will be only slightly different from that of an univalent ion. In this case " k_0 " in Equation (10) will be proportional to $n_2 u$, when n_2 and u denote the valency and the mobility of the ion respectively. For the three ions H⁺, K⁺ and Na⁺, " k_0 " is approximately proportional to their mobilities, cf. equations 10 and 13 (a).

Considering the simplifying assumptions made and the experimental difficulties involved, the agreement is as good as can be expected. The neutralisation of the charge of a colloidal particle by electrolytes is thus mainly the result of electrical "forces."

At the surface, however, the oppositely charged ions which are attracted are subject to the chemical affinity of the surface atoms. The order of adsorption deduced from Equation (10) will not hold for these cases. The order will be determined by the chemical affinity of the surface atoms. The alkali metal cations conform best with the theoretical series. This is in agreement with the fact that they have the least pronounced tendency to form complex "ions," to enter into combination with other elements to form "groups" and to form insoluble salts—all these facts point to their being least affected by "chemical affinity." Their chemical activity is simply due to their tendency to pass into "ions."

SUMMARY

1. The charge of a number of suspensoids has been traced to the adsorption of a common ion. The nature of the chemical forces to which this adsorption is due has been defined.

2. The effect of the electrical charge of a surface (due to the disorption of ions) on "ions" of opposite sign has been theoretically investigated for the case when chemical action does not take place between the surface and the "ion." It has been shown that the "electrical" forces are sufficiently strong to account for adsorption.

The stability of the adsorption of an ion of opposite sign by electrical forces has been given a quantitative form assuming that the charge of the surface consists of "ions" which can be treated as "point" charges widely separated from each other. Actual calculations justify this assumption.

3. The reversal of the charge by electrical adsorption has been discussed.

4. The following series of the order of adsorbability of cations by a negatively charged surfaces has been deduced from the theory.

$\text{Th} > \text{Al} > \text{Ba} > \text{Sr} > \text{Ca} > \text{Mg} > \text{H} > \text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}.$

5. This is the order of the precipitating power of these ions for a number of suspensions of widely different chemical properties.

6. Equations deduced from the theory satisfactorily agree with the experimental observations of Elissafoff on electro-endosmose.

7. The chemical affinity of the surface atoms is not always negligible. For this reason the series given in paragraph 4 cannot be expected to hold in all cases. Equation (10) is applicable to this case also and retains the same form.

My best thanks are due to Professor F. G. Donnan, C.B.E., F.R.S., for his kind interest and advice, and to my friend Dr. J. C. Ghosh.

Physical Chemistry Laboratory,
University College,
Gower Street, W.C.1,
London.

ELECTRICAL THEORY OF ADSORPTION

BY

W. HARRISON, M.Sc., F.I.C.

The paper by Mukherjee dealing with the development of Langmuir's theory of adsorption is of considerable interest and importance and leads to some new ideas.

Recent work has shown that all atoms consist of positively charged nuclei associated with or surrounded by negatively charged electrons. Crystals have been shown to consist not of molecules bound together by some unknown chemical force, but of atoms held together by electrical forces. While there are examples such as that of alumina crystals, in which atomic groupings which might be considered as molecules are arranged in a regular manner, the distribution of electrons cannot be the same in any such grouping isolated from the crystal as within the crystal itself. Within the crystal the electrons are arranged so as to bind the atoms together in three dimensions. At the surface of the crystal, the electrons must be arranged to hold the atoms together in two dimensions, hence they are able to rearrange themselves for the accommodation of other atoms not necessarily the same as those already present. The formation of crystals with alternate layers of ammonia, alum and chromium potash alum by successive growth in solutions of the two compounds illustrates the above point. It is thus clear that a new surface may be formed by contact of a crystal with a solution.

There seems no reason to limit this argument to crystals where the atoms are oriented and the electric forces distributed so as to give strong combination. It will apply, and perhaps more correctly, to non-crystalline substances where the irregular orientation of atoms allows greater freedom for the rearrangement of electric forces.

Physicists having proceeded so far with the electrical explanation of chemical phenomena it appears to the writer unnecessary to go back to chemistry for the explanation of an electrical phenomenon.

It is not necessary, for instance, to assume that the electric charge at the surface of an adsorbent is due to chemical combination of the adsorbent with the ion. It is, of course, known that for most suspensions the charge is of the same sign as that on the ion the substance has in common with the stabilising electrolyte, but stabilisation also occurs where there is no common ion, in which case the charge depends on the nature of the adsorbent and of the ions present. The colloidal metals form examples of this kind.

It is clear that the electrical equilibrium between two substances of different degrees of ionic or electronic saturation must necessarily be different from the equilibrium of electric charges at either of the two surfaces when not in contact, hence when contact occurs there will be a redistribution of electrical forces resulting in a difference of electrical potential.

In a solution electrical charges are always associated with ions, hence the above argument in no way modifies the equations of Mukherjee.

Mukherjee is of the opinion that the collisions of ions due to osmotic forces are comparatively negligible, and that the ions of the same sign as the colloid have very little influence. It is, of course, obvious

that when the charge becomes neutralised the osmotic forces do come into play. The probability that a particular point on the contact surface becomes neutralised is the probability that an ion of opposite sign becomes fixed. This is also the probability that osmotic forces come into play at that particular point. The magnitude of this probability $1 - e^{-W/KT}$ is by no means small as will be seen from Table 2 of Mukherjee's paper, moreover it increases with the valency of either or both of the ions. In general, the effect of polyvalent ions is greater than that of monovalent ions, hence it is to be expected that a polyvalent ion of the same sign will increase the electric charge.¹ This was found to be the case by the writer when making experiments with cotton.

The electric charge had the following values in N/1000 solutions of salts :—

NaCl	Na ₂ SO ₄	Na ₃ PO ₄	NaOH
·0183	·0219	·0240	·0306

The anomalous effect of NaOH is undoubtedly due to the great mobility of OH ions.

The equation 13A of Mukherjee applies very well to some experiments made by the writer in 1912 (*Journ. Soc. Dyers and Cols.*, 27, 279, 1911 ; 34, 91, 1918).

Cotton—Hydrochloric acid solution

Concentration.	Observed E.M.F.	Calculated 13A.	Calculated empirical equation. E = ·0081 log C — ·0157.
	Volts.		
1×10^{-4}	·0168	·0168	·0167
2.5×10^{-4}	·0138	·0136	·0135
5×10^{-4}	·0111	·0110	·0110
1×10^{-3}	·0085	·0085	·0086
2.5×10^{-3}	·0055	·0059	·0053
5×10^{-3}	·0028	·0044	·0029
1×10^{-2}	·0016	·0032	·0005

Maximum - ·0220

With cotton and aluminium sulphate the results calculated from concentration were quite out of relation with the observed results, but when calculated from conductivity by equation 13, substituting 2 for n_2 and 3 for n_1 , the results were much nearer to those observed.

Cotton—Aluminium-Sulphate Solution

Concentration.	Conductivity.	Observed E.M.F.	Calculated 13.	Calc. Empirical. E = ·0064 log K + ·0219.
1×10^{-4}	1.44×10^{-5}	·0092	·0092 (92)	·0091
2×10^{-4}	2.37×10^{-5}	·0078	·0072 (68)	·0077
5×10^{-4}	5.4×10^{-5}	·0055	·0045 (38)	·0055
1×10^{-3}	9.8×10^{-5}	·0036	·0030 (24)	·0037
2×10^{-3}	16.2×10^{-5}	·0025	·0020 (15)	·0024

values between

5×10^{-3}	32.3×10^{-5}	— ·0020 and + ·0016
1×10^{-2}	56.5×10^{-5}	— ·0075 and + ·0043.

The values in brackets are calculated from 13 C.

The writer considers the double layer as consisting of a surface of rigidly fixed atoms under continuous bombardment of positively and negatively charged ions, any particular point on the rigid surface becoming in turn negative, neutral and positive, these conditions arising in any order. The observed contact difference is the average effect of these conditions. Where several kinds of atoms are present in the solution the average number of any one of them at the surface will depend on their concentration, valency and mobility.

The variation of contact difference from negative to neutral and positive was observed with cotton and aluminium sulphate near the neutral point. These variations occurred during the same experiment, the readings being direct measurements of E.M.F.s developed by filtration under pressure.

¹ This point would be covered by putting $n_2 = 1$ and $n_1 = 2$ or 3 in Mukherjee's equation No. 13.

COAGULATION OF INORGANIC SUSPENSIONS BY EMULSOIDS

BY

WILLIAM CLAYTON, M.Sc.

The mutual precipitating action of two oppositely charged colloidal sols has been investigated particularly in the case of the mutual precipitation of dyestuffs and also as regards the influence of certain organic colloids on basic and acidic dyestuffs. The general law deduced from such work is to the effect that oppositely charged colloids precipitate one another only when present within a certain range of concentration ratios, and only then if adsorption takes place.*

The precipitation of suspensions by electrolytes has also been extensively studied and instances are also recorded where a *non-electrolyte* like urea can effect the coagulation of certain colloids. The case of the precipitation of suspensions by emulsoids, however, is very vague, and in fact it is usual to find that "water-peptisable colloids like gelatin, gum arabic, dextrin, soap, or saponine, will peptise many precipitates, and they are often called protecting colloids because they prevent the agglomeration and consequent settling of finely-divided precipitates."²

The present paper describes experiments in which several exceedingly stable inorganic suspensions were, with remarkable rapidity, completely precipitated by small amounts of emulsoids, even though in certain cases the electric signs of the two colloids were identical.

A novel feature, too, was the fact that in every instance the added emulsoid solution causing precipitation was a frothing one, *i.e.*, capable of lowering the surface tension of water.

The more detailed results have been carried out with a stable suspension of an inorganic solid* in dilute HCl, which was very rapidly precipitated by a starch solution, a clear supernatant liquor being soon left above a heavy coagulum. The suspensions investigated contained 10 per cent. of solid and only 0.025 per cent. starch was required.

As one gradually adds the starch solution, stirring continually, a point is very suddenly reached, when the suspension clots into larger particles, which on ceasing stirring, sink very quickly indeed.

A suspension of the solid in pure water is also precipitated by a solution of starch in the same manner. This is inexplicable so far, because in water alone both the solid and starch are negatively charged. (See Table 1.)

* Owing to commercial reasons, the name of this particular substance cannot be divulged. The solid was unaffected by heat, and in boiling water did not undergo change of any kind. The effects described in this paper cannot be attributed to any chemical change or reaction on the part of the solid substance.

TABLE 1
Cataphoresis Experiments

Substance.	Medium.	Charge on Substance.	Substance migrated to
" Solid "	Pure water	- ve	Anode.
" "	Dil. HCl	- ve	"
Starch	Pure water	- ve	"
" "	Dil. HCl	+ ve	Cathode.
" "	Dil. NaCl	- ve	Anode.
" Solid B "*	Pure water	- ve	"

In the case where starch precipitates in acid solution and where the charges are opposite, the small quantity of starch required to effect precipitation is in itself very strange, viz., 0.0025 per cent. of the total solid present.

The previous treatment of the starch is also important. If it is brought into solution by boiling with dilute alkali, its precipitating efficiency is nearly doubled. In actual practice the starch was boiled for 10 minutes in 0.3 per cent. NaOH to make a 1.75 per cent. solution. (In works' practice, this small amount of NaOH had practically no influence on the amount of HCl present.)

It was found that starch made up in alkaline solution precipitated the suspensions independently of temperature. Neutral starch solutions behaved unsatisfactorily as the temperature of the suspension was raised, whilst starch solutions made up in dilute acids were the least suitable for precipitating hot suspensions. (See Table 2.)

TABLE 2
Coagulation by the Use of Various Starch Solutions at Different Temperatures

All Starch Solutions 0.5 per cent. and all boiled for 10 minutes.

Starch.	Nature.	Temperature of Suspension.	Ratio of Starch to Solid.
Rice	Neutral	16° C.	1 : 176
"	"	94° C.	1 : 95
"	Alkaline (0.5% NaOH)	11° C.	1 : 250
"	"	45° C.	1 : 250
"	"	87° C.	1 : 250
Maize	Neutral	16° C.	1 : 125
"	Alkaline (0.5% NaOH)	16° C.	1 : 256
"	"	94° C.	1 : 222

Inspection of the Table shows that whilst rice and maize starches have different precipitating powers in neutral solutions at 16° C., their alkaline solutions have practically the same efficiency and behave independent of the temperature.

* This was another solid, entirely different from the first investigated, and its aqueous suspension was readily flocculated by starch dissolved in pure water.

Other substances investigated were tannin, dextrin, milk, egg albumin, urine, beer and stout—all frothing solutions. With the exception of tannin, all caused coagulation of the suspension in dilute HCl, though a time factor of about one hour was noticed in the case of milk and egg albumin. Urine is an excellent flocculator, being rapid in action, and giving a precipitate of small bulk, in contradistinction to the large “flocks” present in a precipitate due to starch.

Barium sulphate, china clay, talc powder, tin ore slimes, and basic magnesium carbonate, all in sludge states, have also been flocculated by starch solutions, but the exact relationships holding have not been finally settled. Further work is in progress, particularly with regard to basic magnesium carbonate.

DISCUSSION

The precipitation of suspensions by electrolytes is now believed to be due more to selective adsorption of ions than to the existence of electrical charges of opposite signs; also, in general, the colloid adsorbs ions of opposite charge to its own, and the more so the higher the valency.

Here, however, are instances wherein it is difficult to find evidence for the electrical neutralisation view of coagulation; (non-electrolytes in fact, have been very successfully employed) because in certain cases (*e.g.*, starch and “1st solid” in water; starch and “2nd solid” in water), coagulation is effected even though the colloid charges are of the *same* sign.

The difficulty is still further increased by the fact that the coagulants are essentially substances which lower the interfacial tension. Quoting Lewis:—³

“Let us consider substances which lower the surface tension of water, and the interfacial tension between the disperse phase and the medium. The lowering of tension leads of necessity to, positive adsorption. Further, if the interfacial tension between the disperse phase and the medium be lowered by the added substance we would *not* expect coagulation to occur, for the total surface energy is now less than it was before. This is in agreement with Donnan’s theory of emulsification, and is, in fact, the basis of Bredig’s theory of the stability of colloid solutions. But the experiments on suspensions to which reference has been made show that coagulation is actually brought about by substances which lower the interfacial tension. We have here, apparently, a direct contradiction of our previous conclusion.”

These results have been brought forward in the hope of inducing discussion on what for the present, remains a very strange series of results, quite unexpected on theoretical considerations.

¹ Bancroft, *Brit. Ass. Colloid Rept.*, II., p. 13, 1918.

² *Ibid.*, *loc. cit.*, p. 4.

³ *System of Physical Chemistry*, Vol. I., 2nd ed., p. 365.

SOME OBSERVATIONS ON PEPTISATION AND PRECIPITATION

BY

N. G. CHATTERJI AND N. R. DHAR

In his article on peptisation and precipitation, Bancroft (Second B.A. Report on Colloid Chemistry, 1918, p. 2) enumerates a large number of cases of peptisation. We have reinvestigated some of these reactions and come to the conclusion that in several cases the observations are not accurate. Thus we have found that silver chloride, silver chromate, and calcium silicate are not peptised in presence of a concentrated solution of cane sugar. What actually takes place is that, in presence of a concentrated solution of cane sugar or glycerine, the precipitate does not come down immediately. It only does so on keeping for some time. But if it is centrifuged and specially a little diluted, the precipitate settles down at once. It therefore appears doubtful whether peptisation at all takes place in these cases. True peptisation cannot give any precipitate when centrifuged in this way.

We have been successful in bringing about peptisation of a large number of hydroxides by means of glycerine, concentrated solutions of cane sugar or grape sugar. Thus the hydroxides of iron, nickel, thorium, mercury, cobalt, &c., have all been peptised by adding a caustic alkali to the solutions of salts of these metals in presence of glycerine or sugar. In the case of uranium and gold, ammonium hydroxide should be used instead of caustic soda. In none of these cases could any trace of sedimentation be observed even after vigorous centrifuging. One curious fact in this connection seems to have remained unnoticed. It is generally recognised that a substance which can peptise another during the formation of the latter may not be able to do so when once the substance has been formed. We have now observed that not only is the above true, but that peptisation can only be brought about if the alkali hydroxide is added to the mixture of the salt solution and glycerine. On the other hand, precipitation at once takes place if the solution of the salt is added to the mixture of glycerine and alkali hydroxide. Peptisation does not seem to take place in the case of antimony hydroxide, copper fluoride or barium sulphate.

A reference to the literature on the subject of peptisation shows the confusion that exists in this branch of chemistry. The nature of the solutions obtained by dissolving aluminium hydroxide, for example, in alkali hydroxides has been the subject of much discussion. The literature on the subject puts forth evidence in support of both the peptisation and chemical combination views. We have tried to solve the problem systematically by finding out whether any change in electrical conductivity of a solution of caustic alkali takes place when any of the hydroxides is dissolved in it. Incidentally, we have investigated the solubility of the hydroxides of copper, zinc and cadmium in ammonia. We have found that a great increase in the conductivity of the ammonia solution takes place on dissolving these

hydroxides. In this connection, it is interesting to observe that the cobalt-ammonium bases and the chromium-ammonium bases obtained by the double decomposition of a chloride of cobaltamine or chromiumamine by silver hydroxide are fairly strong bases (Cf. Dhar, *Proc. Akad. Wetensch.*, Amsterdam, 1920).

In the case of the action between sodium hydroxide and the hydroxide of copper, chromium, lead, zinc, aluminium, mercury, the following results are obtained. The conductivity of a solution of caustic soda did not appreciably change on the addition of hydroxides of chromium, aluminium, lead, mercury, whilst in the case of zinc the resistance of the caustic alkali solution appreciably increased when zinc hydroxide was dissolved in it. Hence we can conclude that the solutions of aluminium hydroxide, chromium hydroxide, lead hydroxide, mercury hydroxide and copper hydroxide are cases of true peptisation and not of chemical combination. On the other hand, in the case of zinc hydroxide, we get more of chemical combination than of peptisation. Or, in other words, the major part of the hydroxides of aluminium, chromium, copper, lead and mercury exists in sodium hydroxide solution as a colloid, whilst the major part of zinc hydroxide remains as a zincate.

Bentley and Rose (*Jour. Amer. Chem. Soc.*, 1913, **35**, 1490), from their experiments, were led to the conclusion that freshly prepared aluminium hydroxide dissolves in dilute acetic acid to form a colloidal solution. If this be true, our conductivity experiments ought to show no change in the conductivity of the acetic acid solution when aluminium hydroxide is added to it. But if an acetate is formed, the conductivity ought to increase considerably, for acetic acid, being a weak acid, has small conductivity, but its salts are good conductors. As a matter of fact, we have found that the conductivity of an acetic acid solution does not change appreciably when freshly precipitated aluminium hydroxide or ferric hydroxide or chromium hydroxide is dissolved in it, whilst the solution of zinc hydroxide in acetic acid causes a great increase of conductivity. Hence we can infer that the hydroxides of aluminium, chromium and iron become peptised in acetic acid, whilst zinc hydroxide mainly forms zinc acetate with acetic acid. These results are corroborated by the fact that zinc hydroxide is a much stronger base than ferric, aluminium or chromium hydroxide.

We have already mentioned the peculiar behaviour of the products obtained by mixing together a metallic salt (capable of forming an insoluble hydroxide), ammonium or alkali hydroxide, and glycerine or a concentrated solution of sugar. We get or do not get a precipitate of the hydroxide according as we add the salt solution to a mixture of glycerine and hydroxide or the hydroxide to the mixture of the salt and glycerine. The clear solutions obtained in the latter case may be either due to the formation of a soluble compound of the hydroxide with glycerine or a colloidal solution of the metallic hydroxide. If a chemical compound is formed, new ions must appear, and the conductivity of the solution must differ from that of the one in which the metal gets precipitated as hydroxide, even though equal quantities of the reagents are taken in both the cases. But if the clear solutions are formed on account of the peptisation of the hydroxide in glycerine, there is, from the ionic point of view, no difference in the nature of the two solutions, and hence there should be no difference in conductivity of the two solutions.

Here are some experimental results :—

Solution in the Cell.		Specific Conductance.
(1) <i>Cobalt nitrate, glycerine, and caustic soda.</i>		
(a) Cobalt, nitrate glycerine and caustic soda—no pre- cipitate.		·107
(b) The same precipitated	- - - - -	·107
(2) <i>Nickel chloride, glycerine, and caustic soda.</i>		
(a) Clear solution	- - -	·094
(b) Precipitated solution	- - - - -	·094
(3) <i>Mercuric chloride, glycerine, and caustic soda.</i>		
(a) Clear solution	- - - - -	·054
(b) Precipitated solution	- - - - -	·053
(4) <i>Ferric chloride, glycerine, and ammonia.</i>		
(a) Clear solution	- - - - -	·0053
(b) Precipitated solution	- - - - -	·0053
(5) <i>Uranium nitrate, glycerine, and ammonia.</i>		
(a) Clear solution	-	·0021
(b) Precipitated solution	-	·0021
(6) <i>Gold chloride, glycerine, and ammonia.</i>		
(a) Clear solution	-	·0014
(b) Precipitated solution	- - - - -	·0014

We find from the above that the conductivities of the two solutions are the same, and hence the ionic conditions of the two liquids are identical. We can, therefore, say with confidence that the clear solution is *not* due to the formation of any soluble complex, but only a peptised solution of the hydroxide. That they are really peptised solutions is further shown by the fact that a slight rise in temperature brings about a precipitation of the hydroxide, the same change also taking place if the solutions are kept for some hours.

When an alkali hydroxide is added to a solution of a copper salt, a blue hydroxide of copper is precipitated, which on warming becomes black, due, probably, to the formation of a compound less hydrated. But if during precipitation a trace of the copper salt remains undecomposed, the blue hydrate cannot be changed into the black one by any amount of boiling. The undecomposed salt cannot be completely removed by washing with cold water, and it seems probable that the undecomposed salt becomes absorbed by the blue hydroxide and stabilises it. Washing with hot water removes the undecomposed salt, and then the precipitate becomes black. We have observed that if to this black hydroxide a little of the copper salt be added and the whole boiled, a reversible change takes place and the blue precipitate reappears.

The next point for investigation was whether different alkali hydroxides have different actions on the stabilisation of the blue

hydrate or not. In this connection certain striking observations were made. In order to get a rough quantitative idea, 1 c.c. of $\frac{N}{20}$ copper sulphate or copper chloride solution was taken in every case, a measured amount of the alkali of known strength was run in from a burette, and the total volume was made up to 40 c.c. in a boiling tube. The boiling tube was next put in a large beaker containing boiling water, and the time taken by each to turn black was noted. It must be emphasised that this being a case of reaction in heterogeneous medium, the results in some cases could not be exactly reproduced, but on the whole the following conclusions have been drawn from a large number of experiments :—

(1) The stronger the alkali, the quicker is the transformation from the blue to the black modification; thus taking equal concentrations of KOH, NaOH, Ba(OH)₂, Sr(OH)₂, Ca(OH)₂, and aniline, it was observed that KOH blackened first. It was also observed that KOH transformed much more quickly than NaOH.

(2) The behaviour of calcium and strontium hydroxides is very peculiar. Here with an excess of alkali there is more than one stage at which a complete retardation of the change from the blue to the black form takes place. Thus, starting with a slight excess of the alkali, if we gradually increase the quantity, we find that the time taken to turn black gradually increases, reaches a maximum, and then decreases. With very large excess there appears to be a good deal of retardation.

Ammonium chloride and ammonium sulphate seem to retard this change, whilst ammonium nitrate and potassium chlorate are without any influence.

It is well known that in presence of an alkali, the blue freshly precipitated hydroxide of cobalt becomes pink. Now this change is exactly of the same type as the conversion of the blue copper hydroxide to the black variety. In this case also a trace of the undecomposed cobalt salt, nitrate, for example, gets absorbed by the blue hydroxide and stabilises it, and we cannot get the pink variety of cobalt hydroxide if there is a little undecomposed cobalt salt left. Just as in the case of copper, warming of the black variety with a little copper salt regenerates the blue variety, in the case of cobalt warming of the pink form with a little cobalt salt also regenerates the blue variety, but in the latter case the cobaltous hydroxide begins to be oxidised in presence of air.

All those salts which produce a hydroxide soluble in excess of caustic alkali, namely, salts of zinc, aluminium, tin, lead, &c., markedly retard the transformation of both the blue copper hydroxide to the black form as well as that of the blue variety of the cobalt hydroxide to the pink form. It seems probable that the presence of aluminium hydroxide, lead hydroxide, tin hydroxide, &c., in the colloidal state tends to peptise the cobalt hydroxide or the copper hydroxide.

Benedict (*Jour. Amer. Chem. Soc.*, 1904, 26, 695) casually observed that if an excess of a caustic alkali be added to the solution of a cobalt salt, the blue hydroxide which is at first formed does not change into the pink variety if a nickel salt be present. The greater is the retardation, the greater the amount of the nickel salt originally present in the solution. Benedict did not give any explanation of this peculiarity, neither did he mention the action of other salts on

the rate of transformation of the blue to the pink modification. The effect of the presence of salts like ferrous ammonium sulphate, zinc sulphate, manganese sulphate, ferric chloride, chromium sulphate, potash alum, nickel chloride, tin chloride, lead nitrate, cadmium chloride, copper sulphate, magnesium sulphate, calcium chloride, thorium nitrate, strontium nitrate and uranium acetate has been investigated, and it has been observed that only the nickel salt produces a remarkable retardation. The next to produce the greatest retardation seems to be a calcium salt, but there is a great fall in retardation from nickel to calcium. The transformation of blue copper hydroxide to the black variety is also retarded by nickel salts. It is interesting to note that though a soluble nickel salt added to a cobalt salt before the addition of the alkali retards the change of the blue to the pink form, the reaction is not reversed upon the subsequent addition of the nickel salt to cobalt hydroxide. Neither is there any effect when nickel hydroxide is added instead of a soluble nickel salt, though undoubtedly the hydroxide of nickel is formed when excess of alkali is added to a mixture of the salts of cobalt and nickel.

Many interesting cases of adsorption have been observed, we believe, for the first time. Thus, if to the solution of an aluminium salt excess of concentrated alkali is added, the hydroxide at first precipitated redissolves. Now if a few drops of ferric chloride are added, the precipitated ferric hydroxide collected and washed thoroughly with hot water. This ferric hydroxide is now treated with caustic soda and filtered. The filtrate is boiled with ammonium chloride, and a precipitate of aluminium hydroxide is obtained. This is explained by the fact that ferric hydroxide during its precipitation adsorbs some of the colloidal aluminium hydroxide which is not removed by washing with hot water. Similar results have been obtained with a zincate and ferric chloride, and chromium hydroxide in solution and ferric chloride. Again, if to a solution of chromium hydroxide containing an excess of alkali a few drops of magnesium sulphate be added, the precipitate of magnesium hydroxide is found to contain a good deal of chromium hydroxide which cannot be dissolved by sodium hydroxide.

SUMMARY

1. Silver chloride, silver chromate, calcium silicate, cupric fluoride and barium sulphate when precipitated in presence of glycerine or concentrated sugar solutions are not peptised.

2. The hydroxides of iron, nickel, cobalt, thorium and mercury can be peptised by adding a caustic alkali to the solutions of salts of these metals in presence of glycerine or concentrated sugar solution. In the case of gold and uranium salts, ammonium hydroxide should be used instead of caustic soda. In these cases peptisation can only be brought about if the alkali is added to the mixture of the salt and glycerine, but precipitation takes place if the solution of the salt is added to the mixture of glycerine and alkali. Conductivity experiments support these results.

3. The major part of the hydroxides of Al, Cr, Pb, Hg and Cu when dissolved in sodium or potassium hydroxide exists as a colloid, whilst zinc hydroxide mainly forms a zincate, shown from conductivity experiments. Similarly the hydroxides of Al, Fe and Cr form colloidal solutions in acetic acid, whilst zinc hydroxide forms zinc acetate.

4. The transformation of blue hydroxide of copper to the black variety and that of the blue hydroxide of cobalt to the pink form are changes of the same type, and are almost equally affected by different catalysts.

5. The hydroxides of Al, Cr and Zn respectively are adsorbed by ferric hydroxide when the latter is precipitated in presence of solutions of the hydroxides of Al, Cr and Zn in caustic soda.

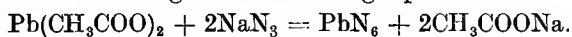
Chemical Laboratory,
Muir Central College,
Allahabad.

THE ABNORMAL CRYSTALLIZATION OF LEAD AZIDE BY PROTECTIVE COLLOIDS

BY

A. G. LOWNDES

Lead azide PbN_6 has been known for some years past to possess all the essential properties of a serviceable initiator of detonation. Both its preparation and manufacture are very easily carried out, all that is necessary being to add a solution of sodium azide to an equivalent quantity of either lead acetate or lead nitrate. In the manufacturing process the acetate is usually employed when lead azide is formed according to the following equation:—



In the laboratory the azide is prepared by running in equivalent solutions of sodium azide and lead nitrate from two burettes into a suitable receiver containing a little water.

Now, the history of preparation and also of the manufacture of lead azide has been a very checkered one. Explosions have been frequent and no very satisfactory cause has been found for them. It has been generally agreed, however, that these explosions are caused by the fracture of large crystals and, although I have reason to doubt this statement, the problem was at the time to produce the azide in such a way that large crystals, and also crystals that were likely to fracture, should not be formed. This problem was at the time being tackled by the research department of Nobel's Explosion Co., Ardeer Factory, Steneston, Ayrshire, N.B., where I was employed at the time doing microscopic work.

Any one who is familiar with microchemical analysis knows that the *bête noir* of all such work is the presence of the slightest trace of a colloid on the microscopic slide which prevents the formation of the normal crystals by which the particular reaction is recognised. On hearing, therefore, of the azide problem, I suggested that the water of the receiver should be replaced by a $\frac{1}{2}$ per cent. solution of gelatin or dextrine. This was accordingly done by the Assistant Manager of Research, Dr. Weir.

The effect of adding the colloid can be seen by reference to the photomicrographs.

Fig. 1 represents a normal manufactured sample, and it will be seen to consist of large partially formed crystals which belong to the Rhombic system. These crystals are really far more solid than they appear, the thickness being considerable.

Fig. 2 simply represents one of these crystals under higher magnification.

Fig. 3 represents a laboratory preparation and shows very perfect crystals, one of which shows a very characteristic twin.

Fig. 4 represents a highly magnified crystal, the twinning of which has given rise to radiating appearance. This kind of crystal was supposed to be the highly sensitive one as it is very liable to fracture on being compressed.



FIG. 1.—Normal manufactured sample.
Magnification 50 diam.



FIG. 2.—Normal manufactured azide.
Magnification 500 diam.



FIG. 3.—Laboratory preparation.
Magnification 50 diam.



FIG. 4.—Laboratory preparation.
Magnification 500 diam.

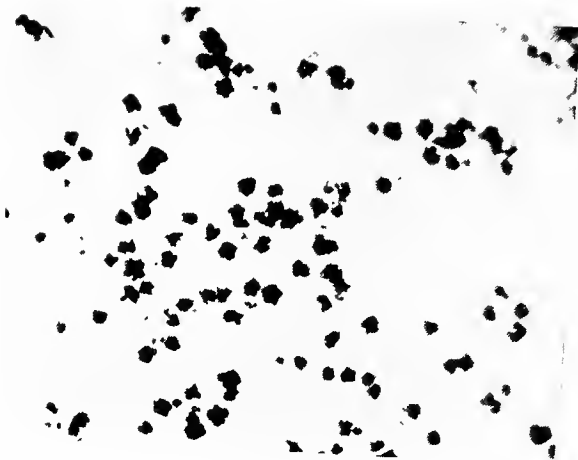


FIG. 5.—Magnification 50 diam.



FIG. 6.—Magnification 50 diam.

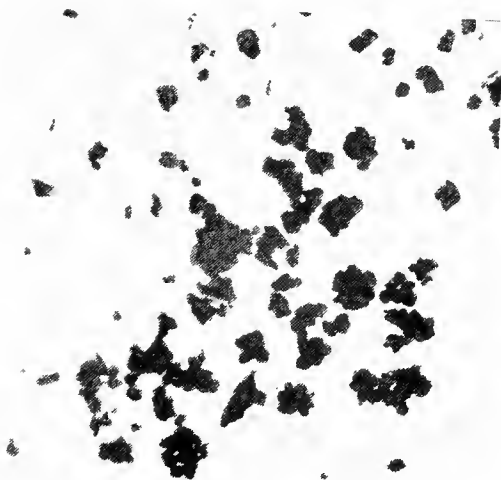


FIG. 7.—Magnification 50 diam.



FIG. 8.—Magnification 50 diam.



FIG 9.--Magnification 50 diam.

Figures 5, 7 and 8 represent the result of adding a colloid to the receiver solution. The products are seen to consist of rounded aggregates with little resemblance to the original crystals.

Fig. 9 represents the result of adding ferric chloride to the receiver solution. It will be noticed that the product is certainly crystalline and from a manufacturing point of view is a quite unsuitable product.

Fig. 6 represents a peculiar crystal that was formed when the receiver solution contained 0.5 per cent. ferric chloride acidified with glacial acetic acid.

It probably consists of a basic ferric azide as microchemical analysis showed it to contain iron.

The crystal was also shown to be insoluble in nitric acid. Further analysis was not carried out since it involved the separation by mechanical means of the crystals on the microscopic slide.

Not only was it essential to prevent normal crystallisation but it was necessary to produce the azide in a homogeneous form, and also in a form that would possess a low angle of flow in order to comply with the necessary conditions of filtration and the further loading of detonators. The necessary conditions were found for producing large quantities of the azide represented in Fig. 8.

ON THE USE OF COLLOIDS IN ELECTRODEPOSITION OF METALS

BY

W. E. HUGHES, B.A. (CAMP.)

It has been stated that the employment of colloids in baths used to deposit metal electrolytically should be avoided. Any such general statement is regrettable, since it is unsupported by facts. The truth is that unless colloids, or substances which produce similar effects to those caused by colloids, are added to some solutions, the metals it is required to deposit from them cannot be obtained at all in a coherent and useful form. A typical example is the solution for lead deposition. In both the hydro-fluosilicic acid solution¹ and the perchloric acid bath,² colloids—glue and peptone, respectively—must be used. If they are not, the deposit will be crystalline, and cannot be obtained in any useful thickness. Again, whether essential or not, it is found that colloidal substances have been added with useful effect to many zinc baths. J. N. Pring and T. C. Tainton³ use gum tragacanth; dextrin forms a constituent of many recipes; a small amount of organic substance (probably glue or gelatin) was found to be present in a very fine sample of zinc deposit, 0.3 to 0.4 inch thick, which lately came to the author from Australia; and L. W. Chapman, in his description of the zinc refining plant at Trail, British Columbia, states that "Glue is sometimes added to the solutions and produces smooth coherent deposits."⁴ Further, it may be mentioned that gelatin or glue is sometimes added in very small amount to the nickel or acid copper solution in order to obtain a very smooth, hard and bright deposit. For certain purposes the addition is useful, since deposits can be thereby obtained which are of such a brightness that they require no buffing after removal from the plating tank, and hence the cost of "finishing" is saved.

The substance used need not always be of an organic nature. Aluminium sulphate, and, sometimes, caustic alkali (especially caustic soda) can, in some cases, be employed in a zinc or tin bath to produce results similar to those effected by colloids. W. D. Bancroft states⁵ that tin salts added to the acid copper bath have a beneficial effect upon the deposit. Many other instances might be given.

It appears, therefore, that the use of colloids is not only not to be avoided, but that in many cases of both plating and refining solutions the employment of them makes it easier to obtain a smooth and coherent deposit, and in some cases they *must* be used in order to obtain a satisfactory deposit at all.

The cause of the beneficial effect of colloids and the like upon electro-deposited metal, considered from the plating or refining point of view, soon becomes apparent upon observation. The deposit, as formed in the absence of such substances, is obviously crystalline in almost all cases. Sometimes the crystals of the deposit are, so to say, *en masse*; sometimes they are isolated skeletons. In the former case, one has a useful, more or less homogeneous, deposit; in the latter case, no useful, coherent deposit is formed. Addition of substances of the kind mentioned causes, in many cases, a change which acts

in the direction of diminishing the size of grain. The change is so extreme in some cases, for example, lead, that the deposit shows, on visual inspection with the naked eye, no sign of structure; it may even appear to possess a bright, polished surface, as in the cases of copper and nickel. Such macroscopic appearances imply hardness in the metal, and often brittleness. Lead is the only metal to form an exception to this association, so far as the author's experience goes. On microscopic examination, however, it is found that the deposit is really crystalline, even where the surface is bright and polished in appearance. The author has never succeeded in finding an instance where this was not so.

Although the change effected by colloids is easily observable in the diminution of the size of grain of which the deposit consists, the way—the *modus operandi*—in which that change is brought about is unknown. The scientific interest of this matter at once appears when it is recalled that, really, one is concerned here with the phenomena of crystallisation and the effect of colloids upon them. So far as pertains to electro-deposited metal, very little work has been done on the subject. R. Marc⁶ and V. Kohlschütter,⁷ working separately, and H. Freundlich and J. Fischer,⁸ in collaboration, appear to be the only investigators who have seriously considered the matter at all in a scientific way. It is notable that these workers give differing views as to the causes that bring about the change in the structure of deposited metal resulting from the presence of colloids in the depositing solution. Freundlich and Fischer say that the change is due to adsorption: Kohlschütter believes that the colloids give rise to colloidal metal. One reason for the prevalent difference of view is that the facts are insufficiently ascertained. There is, in fact, a practically untouched field of inquiry here.

It is, therefore, suggested that on both the practical and theoretical sides, the subject of the use of colloids in solutions employed for the deposition of metals is one of interest and importance, and one to which attention may appropriately be directed during a discussion on the physics and chemistry of colloids and their applications.

¹ A. G. Betts, *U.S. Pat.*, 679, 824 (1901); *Eng. Pat.*, 1,758 (1901); *Met. and Chem. Eng.*, 1903, Vol. 1, p. 407.

² F. C. Mathers, *Met. and Chem. Eng.*, 1910, Vol. 8, p. 350; *Trans. Am. Electroch. Soc.*, 1910, Vol. 17, p. 261.

³ *Eng. Pat.*, 7,255 (1911).

⁴ *Chem. and Met. Eng.*, 1920, Vol. 23, at p. 231.

⁵ *Trans. Am. Electroch. Soc.*, 1912, Vol. 21.

⁶ *Zeit. f. Elektroch.*, 1913, Vol. 19, p. 431.

⁷ V. V. Kohlschütter and H. Schacht, *ibid.*, Vol. 19, p. 172.

⁸ *Ibid.*, 1912, Vol. 18, p. 885.

DISCUSSION

Dr. W. R. Ormandy : I should like to make a few remarks on Mr. Mukherjee's paper, because I think it is one of the most important presented during this evening, in that it deals with some of the fundamental aspects of the broad subject under discussion. The question of the nature and origin of the charge upon colloidal particles is of fundamental importance, and it is unfortunate that, so far, a great deal of the work that has been done upon this subject has been carried out for the most part with exceedingly dilute suspensions, where the error introduced by the ever-present ionised impurities in the water employed may exert a very great influence. Much of the work upon the charge on suspensoid particles is based upon their rate of movement in an electric field. It is generally admitted that, in the absence of free ions in the liquid, there is no movement of the suspended particle in an electric field. It is not so widely realised that the suspended particle may itself carry on its surface a large amount of adsorbed material which could not be removed by any amount of dialysis, but which is set free in the ionised form, if the voltage employed during the measurement of the movement of the particles exceeds a certain limit. I do not think that the present explanation of the movement of suspended particles in an electric field is by any means complete. It seems to me desirable that, wherever possible, the investigations on adsorption and subsequent work on the rate of movement of the particles should be carried out on bodies which in the non-dispersed state are capable of easy microscopic examination, and which can be dispersed until they are beyond the range of microscopic examination. Further, the ideal material would be practically insoluble in water, or when in equilibrium with water would give to the water a constant and low conductivity. I believe that such a material is available in the form of certain types of clay, but for this purpose the china clays, which are essentially crystalline in structure, are not suitable. As at this late hour it is impossible to give the subject the consideration which it deserves, and as I have quite a lot of experimental work dealing with this matter which I hope to publish at an early date. I propose to use the opportunity of such publication for an extended discussion of the paper in question.

Prof. E. F. Burton (University of Toronto) (*communicated*):

In regard to Prof. Mukherjee's reference to the variation in the coagulating power of ions with the concentration of the sol, I may report that there is now in print, to appear in an early number of the *Journal for Physical Chemistry*, an account of work by myself and Miss Bishop, of which the following is a summary:—

With solutions of (1) arsenious sulphide, (2) mastic, and (3) copper (Bredig), it was found that the variation in the coagulative power with the concentration of the disperse phase followed three laws:

(1) For univalent ions the concentration of the ion necessary to produce coagulation increases with decreasing concentration of the colloid—this increase being very marked with low concentration of the colloid.

(2) For divalent ions the concentration of the ion necessary to produce coagulation is almost constant, *i.e.*, independent of the concentration of the colloid.

(3) For trivalent ions the concentration of the ion necessary to produce coagulation varies almost directly with the concentration of the colloid.

This suggests that coagulation is not due merely to simple adsorption of ions, but may be affected by other conditions such as conductivity of the medium and the nature of the ion bearing the same charge as the particles. In particular, it is important to remember that, in the case of all coagulation experiments, when testing the coagulating power of monovalent ions, one always has present ions of the opposite sign of *equal* or *greater* valency, while, in like experiments on trivalent ions one always has present ions of the opposite sign of *less* valency.

Mr. W. Harrison (*communicated*) :

The observation of Clayton that starch, an electro-negative colloid, is precipitated by negatively charged substances such as china-clay, magnesium carbonate, &c., does not rule out the electrical theory of coagulation. In the first place, ordinary starch contains electrolytes which have a strong influence on its properties. (*Compare* Harrison, *J. Soc. Dyers and Cols.*; Samee and others, *Kolloid Chemische Beihefte*, 27, 84, 1911, and 32, 32, 1916; Vols. 3 to 8, 1911-16.)

The fact that alkali increases the coagulating property of starch is important, because starch forms an ionisable compound with caustic soda, and it is most probable that the positive ions from this compound is really responsible for the coagulation of the suspensions mentioned by Clayton.

Mr. J. N. Mukherjee (*communicated reply*) :

Regarding Dr. Ormandy's remarks that the applied voltage may "set free in the ionised form" electrolytes adsorbed on the surface of the colloidal particles, I am rather doubtful whether for the field strengths usually employed (3 to 4 volts per centimetre) there is any justification, either on theoretical or experimental grounds, for the suggestion. At any rate, the numerous observations on the decrease in the migration velocity for the same applied E.M.F. on the addition of electrolytes show conclusively that the electrically adsorbed ions of opposite charge are not set free from the surface by the electrical field. As it is not mentioned how the limiting voltages are arrived at and as their magnitudes are also not given it is not possible to discuss it any further.

I have seen the paper referred to by Prof. Burton (*J. Phys. Chem.*, 1920, 27, 701-15). I would like to draw the attention of Prof. Burton to a paper by myself and Mr. Sen on the same subject (*Trans. Chem. Soc.*, 1919, 115, 461-472) where exactly similar observations have been recorded and which has evidently escaped his notice.

We have further observed that for electrolytes with divalent cations (barium chloride) all the three influences mentioned above can be noticed (*loc. cit.*, p. 465, Table III.). The observations have been satisfactorily accounted for on the basis that we are dealing with two influences :—

(1) the effect of the distance between the particles as affecting their rate of mutual collisions—this factor was first pointed

out by Woudstra in 1908, and v. Smoluchowski has since given a quantitative form.

(2) the change in the amount of colloid-liquid interface with consequent variation in the amount adsorped (*loc. cit.*, pp. 465-468) as originally discussed by Freundlich.

Only arsenious sulphide, copper sulphide, and mercuric sulphide sols were studied. It is interesting to note that mastic and copper sols also show the same effect.

SECTION VI.—ELECTRIC ENDOSMOSIS AND CATAPHORESIS

INTRODUCTORY ADDRESS

BY

ALFRED W. PORTER, D.Sc., F.R.S., F.Inst.P.

I.—ENDOSMOSIS

When a porous diaphragm separates two parts of a liquid through which an electric current is passing, the liquid is often seen to be flowing through the membrane, sometimes towards the anode, but usually towards the cathode. This is electric endosmosis. If a difference of level between the two sides is allowed to be set up the flow ultimately ceases. The phenomenon was discovered by Reuss¹ in 1808, and again, by Porrett² in 1828. It was studied by Wiedemann³ and Quincke,⁴ who observed that the effect is greatest when the liquid conducts badly; that the quantity of the liquid transported is proportional to the current and independent of the width and thickness of the diaphragm, at least, within the limits of their experiments. The amount transported depends not only upon the liquid but also upon the nature of the surfaces in the diaphragm.

On the other hand, when liquids are forced through tubes a difference in potential is set up. The two phenomena are correlative one to the other.

A mathematical discussion of these phenomena was given by Helmholtz,⁵ who showed that both can be explained if an electrical double layer exists at the boundary between two substances, such as the liquid and the porous diaphragm.

Consider the case of a conducting liquid contained in a cylindrical tube. This is the simplest case, because everything will be symmetrical round the axis. For very slow motions the liquid moves in parallel lines (excepting near the ends), and consequently (for an incompressible liquid) the longitudinal velocity u at a given distance r from the axis has the same value from end to end of the tube.

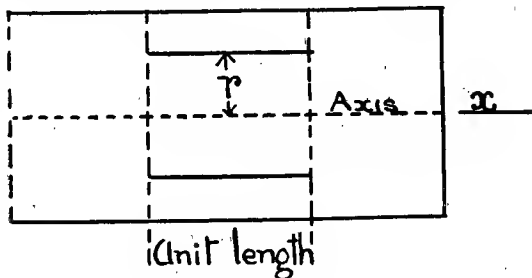


FIG. 1

Let a longitudinal voltage, $V_1 - V_2$, be applied so as to be uniform across the cross section. If there is a charge, q , anywhere in the liquid the force upon it is $-q \frac{\partial V}{\partial x}$. Select any cylinder of unit length and

radius r and let q be the total charge within this cylinder. By the theorem of Gauss the charge q multiplied into $4\pi/K$ (K = dielectric constant) is equal to the total normal electric induction outwards from the surface of the cylinder, i.e., since the electric force outwards from the curved surface is $-\frac{\partial V}{\partial r}$ and the curved area is $2\pi r$

$$-\frac{\partial V}{\partial r} \cdot K \cdot 2\pi r = 4\pi q. \quad (1)$$

Again, if a steady state of flow has been set up, mechanical equilibrium requires that the longitudinal force on the charge $-q \frac{\partial V}{\partial x}$ shall balance the force due to friction against the curved area or

$$-q \frac{\partial V}{\partial x} = -2\pi r \mu \frac{\partial u}{\partial r} \quad (2)$$

where μ is the viscosity of the liquid.

Eliminating q we obtain

$$K \frac{\partial V}{\partial r} = -\frac{4\pi\mu}{\frac{\partial V}{\partial x}} \frac{\partial u}{\partial r}.$$

Now the electric current, C , is equal to

$$-\frac{\partial V}{\partial x} \cdot \frac{A}{\sigma}.$$

where σ = specific resistance of liquid

A = cross sectional area of tube;

therefore

$$\frac{\partial V}{\partial r} = \frac{4\pi\mu A}{K\sigma C} \frac{\partial u}{\partial r}. \quad (3)$$

This equation is independent of the particular distribution of electric charge across the cross-section. If V_a and u_a are the potential and velocity at a point on the axis, and V_w and zero are the corresponding values for the tube wall, it follows that

$$V_a - V_w = \frac{4\pi\mu A}{K\sigma C} u_a. \quad (4)$$

It should be observed that μ , K , σ and C/A are all *specific* quantities.

The meaning of a double layer is that there exists near the surface of the liquid a distribution of electricity of one sign, while an equal quantity of opposite sign exists on the solid. We do not need to enquire too closely into how this charge in the liquid is distributed, provided that it is in the immediate neighbourhood of the surface; or, more precisely, provided that the distance of any of it from the surface is small compared with the radius of the tube. Equation 2

shows that wherever there is no charge, $\frac{\partial u}{\partial r}$ is zero; hence, in

practically the whole tube u then is constant and equal to u_a . The total flow of liquid is consequently $u_a A = U$ (say). Hence, from (4)

$$U = \frac{K\sigma C}{4\pi\mu} (V - V_w) = \frac{KA}{4\pi\mu} \log^1 \text{ voltage} \times \text{trans. voltage}. \quad (5)$$

Here $V_a - V_w$, the transverse voltage, is the drop of potential across the double layer.

The assumptions made in this proof are identical with those made by Helmholtz; but the method of solution is much simpler and the conditions under which equation (4) holds are, I think, made clearer. In addition, the influence of the dielectric constant has been allowed for (Helmholtz took it as unity). This has been allowed for in the routine fashion, although with some diffidence. If it is to be taken as equal to the dielectric constant of the liquid as ordinarily measured, it would seem to require that the charge in the liquid is distributed over a thickness containing a fair number of molecules. This, of course, would be possible without equation (4) being invalidated thereby.

Horace Lamb⁶ discussed the problem afresh, because he was dissatisfied with Helmholtz's application of the equation to thin layers of molecular dimensions. Instead of assuming that n and V vary continuously, he considers that finite slip occurs near the boundary between the liquid and solid. Instead of a friction per unit area at the boundary equal to $-\mu \frac{\partial u}{\partial r}$ he puts a force proportional to the discontinuity in the velocity at the surface. He then confines his attention to the case where the charges are distributed over the surfaces of this discontinuity. I have put forward the proof given above in the hope that it also removes some of the difficulties in Helmholtz's proof.

To calculate the total charge on each face of the double layer, we are on much more uncertain ground. We return to equation (1), where it is given by

$$q = \frac{K \times \text{surface of layer}}{4\pi} \times \text{trans. slope of pot. at wall.}$$

If we write this slope as $\frac{V_a - V_w}{b}$ we define a *mean thickness* b of the double layer. This thickness is probably comparable with molecular dimensions. If it be assumed equal to the distance of two molecules apart in the liquid q can be determined after $V_a - V_w$ has been determined by equation (5) from endosmotic experiments.

But there is no certainty that this assumption is true, and the value of q is uncertain to the same extent.

II.—CATAPHORESIS

Similar double layers are formed at the surface of solid particles immersed in a liquid and relative motion of the particle and liquid takes place when an electric current flows through the liquid. The particle is usually considered to be non-conducting, but this will clearly not be so in the case of metallic suspensions.* Since, in these cases, the solid is easily moved, its motion relative to the liquid, regarded as at rest at some distance from the particle, can easily be observed. This motion is cataphoresis. It was examined by Quincke, and, later, in more detail, by Linder and Picton.⁷ The motion follows from the double layer theory. If an equal opposite velocity to that of the particle is impressed on the whole system, the

* It may then, however, be coated with a non-conducting layer (of oxide, for example), which would make the particle effectively non-conducting. It is doubtful to what extent a colloidal metal is the pure metal.

particle will be at rest while the liquid at a great distance will have a uniform motion, v . Let the gradient of potential driving the current also be uniform at a great distance and equal to G ; both v and G being parallel to x . At a great distance the potential will be given by $V = -Gx$, whereas near the particle additional terms will enter, due to the disturbance introduced by the presence of the particle, which vanish at a great distance. When the motion is slow, the motion will everywhere be irrotational, and in this case can also be derived by differentiating a potential function ϕ and at a great distance $\phi = -vx$; whereas near the particle additional terms will enter, which vanish at a great distance.

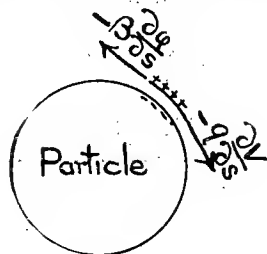


FIG. 2

Now if we follow Lamb in assuming a slip $u_0 = -\frac{\partial \phi}{\partial s}$ at the surface of the particle, the corresponding force due to friction on an element of unit area is $-\beta \frac{\partial \phi}{\partial s}$; the force on the charge on the element is $-q \frac{\partial V}{\partial s}$ and for steady motion $-\beta \frac{\partial \phi}{\partial s} - q \frac{\partial V}{\partial s} = 0$.

This condition is satisfied if we take $V/\phi = \beta/q$ everywhere.

Hence $\frac{G}{v} = \beta/q$ also.

But v is equal but opposite to the actual velocity of the particle, and G is the gradient of potential $-\frac{\partial V}{\partial x}$ in the undisturbed part of the field. Hence, if c is the current per unit area in this part

$$c = -\frac{1}{\sigma} \frac{\partial V}{\partial x} = \frac{G}{\sigma}$$

and therefore $-v = \frac{q\sigma c}{\beta}$.

The radial voltage at the particle is

$q \div$ capacity per unit area
 $= q4\pi b/K$ approximately (for a thin layer), where b is thickness of the double layer.

Also, as before $\beta u_0 = \mu \frac{\partial u}{\partial r} = \mu \frac{u_0}{b}$ whence

$-v = \frac{K\sigma c}{4\pi\mu} \times$ radial voltage in double layer. This is identical with the endosmotic equation, but with reversed sign.

III.—ORIGIN OF THE DOUBLE LAYER

A few words only will be said here in regard to the origin of the double layer. The phenomenon is obviously an example of the preferential attraction of electrons to particular bodies. It is this preferential attraction (the "specific attraction" of Helmholtz) to which ordinary electrification by "friction" is due. The two opposite faces of the bodies in close contact become oppositely charged, thus forming what is, in reality, a double layer, the components of which can be separated by a separation of the bodies themselves. Very small changes in the surface are sufficient to reverse the direction in which the transferred charges go. Roughening a glass surface is sufficient to make it become the negative body against silk. Two pieces of thin celluloid, placed in juxtaposition and passed quickly between the thumb and forefinger, in such a way as to curve them strongly during the passage, become oppositely charged; the one which touches on its convex side becoming positive, as though electrons had "evaporated" or "dissolved" from it more easily. Similarly, between a solid and a liquid, Voltaic differences of potential are set up, being due to a passage of charged ions (*i.e.*, ions carrying electricity with them) across the interface. In this case the preferential attraction for the matter of the solid has to be considered as well as that for the electricity. Similarly, there is specific attraction causing "adsorption" at an interface; and the adsorbed elements may be charged. In endosmosis and cataphoresis we are only concerned with electrolytes, because it is essential that an electric current can flow. When the solid becomes positively charged it may be due to positive ions (either of H in the case of an aqueous solution, or of the cation of the solute) being attracted and forming a sessile layer around it; while the corresponding anions produce a negative region in the neighbourhood. These anions will be attracted to the sessile layer; but they will, no doubt, form a much more mobile region, because it will be more accessible to the shocks arising from the agitation of the molecules of which it is composed. It is for this reason that I have emphasised, in the proofs which form the main theme of this introduction, that the main conclusions do not depend upon the precise distribution of the charges in the liquid (*see equation 4*). The representation of the double-layer by two parallel sheets of charges is, of course, merely the result of the process of averaging which it is convenient to pursue in dealing with such complicated circumstances as those which exist in the body of a liquid.

In a paper to be communicated to this meeting by J. N. Mukherjee, the transitional character of this mobile layer is emphasised and deductions are made from it which seem to deserve very careful consideration.

Finally, it may be well to mention, that the potential-drops across the layer in the case of small particles may very likely be different from those observed at extended surfaces. I am not aware of any evidence on this point. The experiment with curved celluloid, quoted above, illustrates the possibility of the effect being different.

It is, of course, merely a special case of the influence of pressure—the pressure inside the particle being different from that outside

Similar effects arising from the same cause are the variations, with pressure, of solubility and vapour pressure.

University College, London.

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SOME PRACTICAL APPLICATIONS OF ELECTRO ENDOSMOSIS AND CATAPHORESIS

BY

W. R. ORMANDY, D.Sc.

The number of industries which have arisen out of the deliberate application of the theoretical laws relating to electro endosmosis and cataphoresis are comparatively few and there is not much progress to record since the issue of the second report on Colloid Chemistry which appeared in 1918.

The work, which has issued from the laboratory of the Elektro Osmose Aktiengesellschaft, still remains the largest contribution to this class of work. Undoubtedly the Schwerin patents applied to the purification of clay form one of the most interesting practical adaptations of the complicated physical laws dealing with colloids.

The history of the development may be described briefly as follows :—

First the discovery that suspensions of many clays could be so treated by a direct current of electricity as to bring about the deposition of the clay in a more or less dry state on a negative pole. It was found that all clays did not re-act and a second series of patents deal with the possibility of increasing reactivity of the clay particles to the electric current by adding traces of suitable electrolytes which were absorbed by the clay.

Further work showed that even with the addition of suitable electrolytes there were clays which were not amenable to electrical separation or at any rate not in a sufficiently pronounced degree to render the process commercially applicable. A third series of patents was taken out claiming the use of added colloidal substances which would be adsorbed by the clay, which colloidal substances were then capable of adsorbing the necessary electrolytes, and for this purpose such bodies as silicate of soda, humic acid (Casseler brown earth) and the like were employed. Count Schwerin was one of the first to realise the possibility of applying the comparatively new scientific discoveries relating to colloids to industrial purposes. So far as my knowledge goes, he was the first man to recommend the addition of electrolytes, with or without other colloids, to clay suspensions, with the object of converting the clay into the sol condition so that the sedimentation of the heavier impurities might take place. It is impossible by mixing a plastic clay with even a large amount of water to separate the bulk of the impurities without losing a lot of clay substance and without the use of an excessive amount of water. The free silica which is always present in clay is surrounded by clay in the gel form and the separation of this clay from the particle only takes place when suitable electrolytes are added so that the clay is peptised and separated from the silica.

The osmose machine applied to the separation of the suspended particles is an interesting example of the application of comparatively recent physical-chemical laws. In the preparation of the clay we make use of the laws of selective adsorption, of the influence of

adsorbed colloids and finally of the directive effect of an electric current on a suspension of particles in the sol condition. On the anode of the osmose machine the negatively charged particles are deposited and the moment a film of these exists over the anode, brought about by cataphoresis, electro endosmose comes into action and the water in and around the clay is electrically driven through the capillary spaces resulting from the close contact of the clay particles deposited on the anode. It is interesting to note that the amount of moisture remaining in the clay attached to the anode is intimately related to the physical nature of the clay substance. If china clay is being worked upon it will be found that if sedimentation is carried out to such an extent that only 50 per cent. of the clay substance remains in suspension, so that only the finer particles of the clay remain, such a suspension treated on the osmose machine will give a product containing approximately 28/32 per cent. of water. If the china clay which has settled out be now remixed with water and passed through the osmose machine—that is, if we make use of the coarser clay particles only—the osmose machine will yield a product containing 35/40 per cent. of water. On the other hand, if similar experiments be carried out with a very plastic ball clay having much finer particles in the sol suspension, the osmose machine may deliver a product containing as little as 18 per cent. of water. It would appear as though the percentage of water in the clay delivered from the osmose machine were due in some measure to the fineness of the state of division in the sol state and to some extent also it is a measure of the plasticity.

In treating a very pure specimen of a well-washed English china clay by the osmose process, it has been found possible to deposit as much as 6,833 kilogrammes of dry clay substance with 11.8 kilowatt hours of current when working at 50 volts pressure..

It is interesting to regard this deposition of clay by direct electric current as though we were dealing with the deposition of copper from a solution of one of its salts. On the basis of the figures given above, we should have to assume that the equivalent weight of china clay was of the order of 700,000 and that where a given current would deposit 1 gramme of hydrogen or $31\frac{1}{2}$ grammes of copper, it would deposit 700,000 grammes of clay. Needless to remark, these figures can only be obtained when working with a very pure clay and with water of very low conductivity.

It has been stated that the electro-osmotic process does not bring about any purification of the clay material in the actual osmose machine, but, whatever may be the position theoretically, the fact remains that in practice such a purification is brought about, as has been proved beyond all doubt at the laboratory of the Osmosis Company, Limited, by Mr. Lawrie, when working on tons of china clays and ball clays.

PEAT

The application of the electro-osmose filter press to colloidal peat suspensions results in the removal of large quantities of water at a comparatively low cost in fuel; thus hydraulically mined peat, containing only 5 parts of dry peat substance in 100 parts of suspension, results in the removal of 85 parts of water from the 100 parts of mixture, with an expenditure of current which can be produced by the consumption of one-sixth of the resultant fuel. The ultimate drying of the product from the filter press containing

1 part of peat to 2 parts of water is comparatively simple, but the difficulties attached to the use of the process are more largely mechanical. Unfortunately peat is generally found in comparatively thin layers, and owing to the small percentage of dry substance contained in the peat, the osmose plant would soon be far distant from the point where the fuel was being worked. It is obvious that the process lends itself particularly to application in countries where water-power is available for producing the necessary electricity.

COLLOIDAL SILICA

By passing an electric current through silicate of soda solutions it is possible to drive out the soda and leave the silicic acid behind, but this can only take place if diaphragms are employed which will permit of the soda ions passing out of the silicate of soda solution and will not permit of backwards way diffusion into the inner chamber. Years of experiments have resulted in the development of such diaphragms, and it is now possible to produce silica solutions up to 30 per cent. in strength,* but the stability of these solutions diminishes as the concentration increases. It is interesting to note that the stability of these silica solutions has been found to increase with each step in progress which has been made, resulting in the more complete removal of the sodium salts. These silicic acid solutions of 5/10 per cent. strength have been largely used on the Continent for therapeutical purposes, and the strong solutions after polymerisation result in the formation of a gel, which, on drying, produces an inert highly electro-negative finely divided colloidal gel, which has proved to have extraordinary properties as an adsorbent for use on wounds. In the Third Report on Colloid Chemistry, page 123, there is a reference to a statement by W. Ostwald "that fresh colloids (particularly silica) will pass through a membrane, but after keeping a few days they will not pass through." It adds "there is no connection between the rate of diffusion through the membrane and the molecular weight." It has been found that the silicic acid solution produced by the electro-osmose process, at the moment of its preparation, has a molecular weight corresponding to the formula H_2SiO_3 , and that the molecular weight increases steadily with the time, until with a 10 per cent. solution, after about 6 weeks, the molecular weight has reached something in the order of 60-80,000, and obvious separation takes place. If a 10 per cent. solution of silicic acid be kept in a vessel lined with paraffin wax, it is possible, by means of conductivity experiments, to determine the age of the preparation to within a few hours. It would seem likely, therefore, that the ability of new solutions to diffuse through a diaphragm is directly and closely connected with the molecular weight. No doubt Ostwald's less pure solutions polymerised to such an extent in a few days that they could no longer pass through a diaphragm.

TANNING

It would appear that a very great simplification has taken place in the plant now used for electric tannage of skins. Two factories in Germany are at present employing the process, and the chief claim made is that it permits of the utilisation of very dilute tanning liquors, with complete utilisation of the tanning material. It is further claimed that experiments have shown that it is preferable to complete the tanning for two or three days in the ordinary way in strong

liquors, and that the current consumption is thereby reduced from 20-25 kilowatt hours per square metre of hide, when complete electrical tanning is employed, to 6 or 7 kilowatt hours per square metre when finishing in strong liquors is employed. Here, again, progress has resulted entirely from the discovery of suitable membranes for the enclosing of the anode and cathode.

ORE SEPARATION

It has been found that if a finely ground ore be suspended in water, that in many cases it is possible to add traces of electrolyte which are selectively adsorbed. If such finely ground ore be allowed to fall through a column of water to which has been added the necessary quantity of suitable electrolyte, and if a current be passed through the water at right angles to the path of the falling particles, the charged particles are drawn on one side and fall into separate receptacles, bringing about concentration of the ore.

Iron ores occurring in clay deposits have been concentrated by the removal of the clay substance on the lines above described.

ANTI-DIPHTHERITIC SERUMS

It has been found that the anti-toxin contained in the blood serum of a horse is combined, for the most part, with the para-globulin, very little being combined with eu-globulin, and practically none with the fibrinogen. It has proved possible by using suitable diaphragms to separate from the anti-diphtheritic serum of the horse a pure para-globulin containing the bulk of the anti-toxin previously present in the serum. Such anti-diphtheritic globulin is free from amino acids, and from the decomposition products of the albumen bodies such as albumose and peptones, and bodies containing ferments such as katalase, enzymes and the like. Furthermore, it is claimed that the anti-diphtheritic product so prepared is free from toxon. It has been urged that anti-diphtheritic serum of a horse may, and probably does, contain toxins which have been combined in a weak way with anti-toxins, and that these compounds may split up in the human body with the setting free of toxins which may lead to, and be the cause of, the dangerous secondary symptoms which so frequently occur after serum injection. It is claimed that the electro-osmose process separates the toxon as such, as well as splitting the compound of toxin and anti-toxin with separation of the toxin. The resulting pure anti-toxin para-globulin has a concentration six to ten times that of the best horse serum.

GELATINE

By the use of diaphragms very similar to those employed for the separation of the constituents in serum, it has proved possible to prepare exceedingly pure gelatines from low grade gelatine, and even from glue. These gelatines are so pure that a 5 per cent. solution may be kept for weeks or months without any bacterial growth occurring therein, owing to the fact that the whole of the food material which is necessary for bacterial growth has been so entirely removed. Such gelatine is being prepared in this country, and is being tested for photographic and other purposes.

REMOVAL OF OIL FROM WATER

The electrical methods which are employed for the removal of oil from watery emulsions is really an application of cataphoresis. The oil globules are charged by adsorption of the inorganic salts present in traces, and pass to the anode.

Dewatering of Oils.—It is well known that many tars produced by distillation and many natural paraffin oils contain water in a state of emulsion which is very difficult to separate. Just as the application of direct current electricity has for some time been employed as above stated for the separation of oil emulsions from water, so similar electrical methods are used for the removal of the water particles forming the disperse phase in oil as a continuous phase. This application is very largely used in the Californian oilfields.

The following contribution to this Section was received from Professor Dr. H. Freundlich (Berlin-Dahlem), in response to an invitation:—

THE EFFECTIVE POTENTIAL DIFFERENCE OF ELECTRO-OSMOSIS AND ALLIED PHENOMENA

BY

H. FREUNDLICH (Berlin-Dahlem)

The nature of the potential difference at work in electro-osmosis, kataphoresis and allied phenomena—which I group as electrokinetic—is not as yet fully understood. On the theory of *Helmholtz*¹ of the electron double layer we can satisfactorily represent the physical aspect of the processes. But the relation between this electrokinetic potential difference ζ and the ordinary *Nernst* potential difference ϵ , with which we deal so successfully in the theory of galvanic couples, is not by any means clear yet. We might best solve this problem by measuring simultaneously, at the same wall, both the potential differences ζ and ϵ . In the case of metals, for which ϵ is so well known, unobjectionable measurements of ζ are not easily obtained. The kataphoresis of metal sols is objectionable because we are doubtful as to the state of the surface of the metal (its oxidation, &c.). It would therefore appear preferable to measure ζ at the interface glass-aqueous solution. ζ may reliably be determined by the aid of electro-osmosis, or of stream potentials in glass capillaries. But *Haber* and *Klemensiewicz*² have demonstrated that there is also a *Nernst* p.d. at their “glass electrodes.” In conjunction with *Rona* I have, therefore, determined, in the first instance, the stream potentials in glass capillaries, and in the second instance the *Nernst* p.d. at a glass electrode (made, as far as possible, of the same glass) after *Haber* and *Klemensiewicz*.

In measuring the stream potentials we made use of a capillary of an easily-fusible Thuringian glass, 10 cm. long, about $\frac{1}{3}$ mm. in diameter, through which the aqueous solution was forced by the pressure of the nitrogen in a cylinder. The experiments are conveniently and smoothly performed, provided the electrodes be as reversible as possible. Our electrodes were 0.1 N. calomel electrodes; they were joined to the ends of the capillary through tubes charged with a 3 per cent. agar jelly prepared from 0.1 N. solution of KCl. A binant electrometer served for the measurements.

In complete agreement with previous experiences³ we found the concentration of the electrolytes to be of decisive importance. In concentrations exceeding about 1,000 micromols (millionth parts of a mol) stream potential could no longer be observed; generally concentrations of from 10 to 100 micromols suffice to reduce the ζ of pure water to very small values.

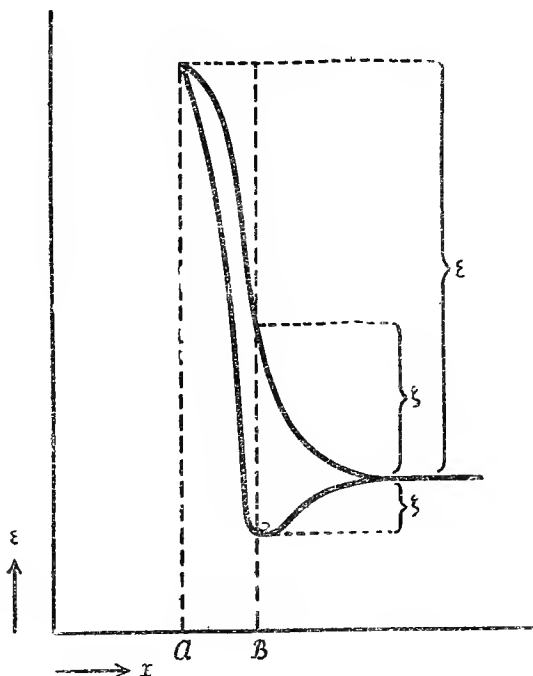
The effect depends essentially upon the kations, their valency and other properties, which we may connect with their adsorbability. Salts with univalent kations such as NaCl, KCl and others are the least effective; salts with bivalent kations, and further also acids, are considerably more effective. With none of these it was, however, possible to reverse the negative charge of the glass into a positive

charge. But this reversal is produced by aluminium chloride already at a concentration of 1 or 2 micromols (*i.e.*, about 0.15 mg. per litre), further by crystal violet at about 50 micromols. The reversal with aluminium chloride was also observed when there were present in the solution 150 micromols of KCl in addition to 6 micromols of AlCl_3 .

The measurements at glass electrodes were carried out exactly as previously by H. and K. A globe of very thin-walled glass dipped into a beaker filled with the electrolyte solution, these solutions being the same as those used for the stream potentials. The glass globe contained 0.1 N. solution of KCl and in it a platinum electrode joined to the binant electrometer. In the beaker was the earthed 0.1 N calomel electrode. Before each series of measurements we repeated the H. and K. sequence of experiments with solutions of H^+ and OH^- ions of various concentrations to make sure of the applicability of the method.

It resulted that we did not find anything, in the experiments after H. and K., of the peculiar effects observed with stream potentials. When the electrolyte solution contained, *e.g.*, 100 micromols of KCl, and we added hydrochloric acid in concentrations increasing from 5 up to 50 micromols, we observed electrometer deflections up to about 50 millivolts, in the sense of increasing acidity. When we took aluminium chloride of the same molar concentration, in the place of HCl, we observed deflections in the same sense attaining 40 millivolts, whilst crystal violet yielded only a small deflection of about 15 millivolts even at a concentration of 200 micromols.

The glass electrode after H. and K. behaves altogether like an H^+ electrode. Since the H^+ ion concentration is badly defined in solutions so poor in electrolytes, one cannot well expect to obtain exactly reproducible results. For this reason the same experiments were repeated with buffer mixtures (of sodium acetate and acetic



acid). The electrometer deflection, observed with a buffer-mixture of a definite H^+ ion concentration, was not in the slightest way changed by the addition of aluminium chloride and of crystal violet in concentrations up to 100 micromols. It follows from these experiments that ζ and ϵ are certainly not identical. We must, on the contrary, assume that there is a space charge at the solid interface, a diffuse double layer (after *Gouy*⁴) which projects rather deeply into the liquid. ζ represents the part of the double layer which lies entirely in the liquid, that is to say, the p.d. between the liquid film adhering to the wall and the movable liquid. On the other hand, ϵ is the p.d. between the acid wall itself and the interior of the liquid. The annexed diagram illustrates the relation. The ordinates represent the potentials, the abscissæ the distances from the solid wall, measured in the liquid. The fixed wall is on the left of A; between A and B is the film of liquid adhering to the wall; to the right of B the movable liquid. The diagram shows that with the possible variations of the potential curve, ζ may even differ from ϵ in sign.

Since ζ lies entirely within the liquid we have according to *Pellat* and *Perrin*⁵, and in distinction from *Helmholtz*, to take the dielectric constant into consideration. When we then calculate the p.d. ζ after the formula of *Helmholtz*, $\zeta = 4 \pi \eta \lambda E / p.D.$ ⁶, we find values up to about 100 millivolts, smaller therefore than the ϵ values, as we should indeed expect on our assumption. The potential ϵ being, in the experiments of H. and K., quite independent of ions such as those of aluminium and crystal violet, we understand why nobody, in taking p.d. measurements after Nernst at metallic electrodes has ever noticed any influence of the valency and adsorbability of such foreign ions, whilst that influence completely dominates the phenomena of electro-kinetic processes.

When we attempt to explain the influence of electrolytes upon the p.d. ζ , we have to bear in mind that according to *Gouy*⁷ the thickness of the film projecting into the liquid decreases strongly as the concentration of the electrolyte increases. With higher concentrations the film soon becomes so thin and penetrates to so small a depth into the liquid that we can, in electrokinetic experiments, no longer separate the two coatings from one another. This point and the increasing conductivity of the solution account for the vanishing of the electrokinetic effect at higher electrolytic concentrations. With respect to the influence of the nature of the ions we seem to be constrained to ascribe importance to the adsorbability and to the valency essentially in connection with the adsorbability.⁸ It is noteworthy that we meet with this striking effect of the aluminium ion and of other ions of high valency not only in electrokinetic experiments at glass walls, but also at phase boundaries of entirely different nature. We find it, to quote a few examples, in the kataphoresis of little droplets of hydrocarbons⁹ and of air bubbles,¹⁰ further in the coagulation—which, we know, is intimately connected with electrokinetic processes—of arsenic trisulphide,¹¹ and of gold¹² and silver sols,¹³ &c. The facts suggest that we have in all these cases to deal with a distribution of the ions, depending upon the nature of the ions, in the layers of water directly adhering to the different phases.

There are, moreover, also electrochemical phenomena in which both ϵ and ζ come into play. Such are the capillary-electric phenomena at the interface mercury-aqueous solutions. The limiting surface tension of mercury is certainly not merely to be interpreted as a function of the potential difference and thus of the mercuric ions

which determine the p.d. The distribution of the ions in the water-film adjacent to the mercury surface will certainly influence the surface tension.¹⁴ When now we have ions present of pronounced adsorbability and consequently deal with a characteristic ζ , the maximum surface tension will not be attained at the same potential as in the presence of capillaryly-active electrolytes; we thus find a displacement of the maximum of surface tension. It is in accord with this view that the maximum of capillaryly-active ions of opposite charges is displaced also in the opposite direction.¹⁵ Experiments made by myself and Miss Wreschner, Ph.D., show that basic and acid dyes which are so effective in electrokinetic phenomena, are prominent also in this respect. Kations of basic colouring matters, like other kations which are capillaryly-active, displace the maximum towards the ascending positive branch of the curve of electrocapillarity; anions of acid dyes, like other capillaryly-active anions, shift the maximum over to the descending negative branch. This displacement will also be noticeable at higher electrolytic concentrations, at which ζ has only small values; for the effect of the potential gradient lying in the liquid may still be very marked, although we measure only small potential differences in electrokinetic experiments owing to the high conductivity concerned. That the maximum of such capillaryly-active ions is not only displaced, but actually lowered, accords with the fact that capillaryly-active substances may lower any interfacial tension.¹⁶ In electrolytes, the anions and kations of which are both particularly inactive as regards capillarity, the p.d. is zero for the maximum of surface tension. This condition occurs for mercury in a solution of KNO_3 ; in this instance the electrocapillary curve deviates merely by a few tenths of one per cent. from the parabolic shape—in accordance with the *Lippmann-Helmholtz* theory.¹⁷

Looking back, we may answer the question raised in the introduction in the sense that the *Nernst* potential difference ϵ is by no means identical with the electrokinetic p.d. ζ . The *Nernst* potential ϵ represents the total difference between the interior of the first phase and that of the second phase; the electrokinetic potential ζ represents that portion of the difference which falls within the displaceable liquid layers.

¹ *Gesammelte Abhandl.*, I., p. 855.

² *Zeitschr. Physik. Chem.*, **67**, 385 (1909).

³ Kruyt, *Kolloid Zeitschr.*, **22**, 81 (1918); also v. Elissasoff, *Zeitschr. Physik. Chem.*, **79**, 385 (1912), "Electro-osmosis in Glass Capillaries."

⁴ *Journ. de Phys.*, **9**, 457 (1910).

⁵ *Journ. de Chim. Phys.*, **2**, 601 (1904).

⁶ p = excess pressure forcing the liquid through a capillary in a Poiseuille stream; E = p.d. between the electrodes; η = viscosity of the liquid; D = dielectric constant; λ = specific conductivity.

⁷ *Loc. cit.*, p. 5.

⁸ Freundlich, *Kapillarchemie*, pp. 243, &c. (1909).

⁹ Powis, *Zeitschr. Physik. Chem.*, **89**, 91 (1915).

¹⁰ McTaggart, *Phil. Mag.*, [6], **27**, 297 (1914).

¹¹ Freundlich, *Zeitschr. Physik. Chem.*, **44**, 129 (1903).

¹² v. Elissasoff, *loc. cit.*, p. 2.

¹³ Burton, *Phil. Mag.*, [6], **12**, 472 (1906).

¹⁴ Gouy, *Ann. d. Chim. et d. Phys.* [7], **29**, 145 (1903); [8], 3, 291 (1906); [8], 9, 75 (1906). Freundlich, *Kapillarchemie*, pp. 187, &c. (1909).

¹⁵ Gouy, *loc. cit.*, note 6, p. 8.

¹⁶ Freundlich, *Kapillarchemie*, pp. 187, &c. (1909).

¹⁷ Krüger, *Zeitschr. Elektrochem.*, **19**, 617 (1913).

DISCUSSION

Prof. J. W. McBain : It is an almost necessary corollary to the theory of colloidal electrolytes that electrical endosmosis is due entirely to the free ions of the double layer, that is, that the charges involved are due to the adsorption of one ion which is thereby fixed upon the surface, leaving its partner as an ordinary ion, somewhere in the neighbourhood, but free to move in an electric field, carrying its water of hydration with it, and possibly also the solution itself through friction or viscous drag.

Mr. Darke has been carrying out some measurements in the Bristol laboratory to test this explanation of electrical endosmosis. Although I can only refer to preliminary results which must be accepted with all due reserve, pending the use of improved apparatus, nevertheless, these preliminary results are sufficiently striking to be referred to here.

Mr. Darke finds, first, that the conductivity of a solution of potassium chloride is about 9 per cent. greater when measured in coarse capillary tubes of fused silica of about $\frac{1}{4}$ mm. diameter, than when it is measured in bulk in the open. This extra 9 per cent. of conductivity is, according to our view, to be ascribed to the extra potassium ions, equivalent to the chlorine ions which have been adsorbed; that is, we have the conductivity corresponding to the average bulk concentration of the potassium chloride, superadded to which comes the conductivity due to the excess of the potassium ions. This increase is only observed after repeated rinsing with fresh solution; the effect initially observed is, of course, in the opposite direction.

A second interesting result follows from these observations when we calculate the amount of chlorine ions which have been adsorbed upon the surface of the silica. Assuming a density of 2 for the surface film, which is the density of solid potassium chloride where the potassium and chlorine ions in the space lattice are equally responsible for the volume and density, we find that the amount of chlorine ion equivalent to the excess of free potassium ions, as deduced from the conductivity experiments, is just sufficient to cover the surface of the fused silica with a layer of chlorine ion one molecule deep.

Our next step has been to attempt some approximate absolute measurements of electric endosmosis for, as far as I know, none such exist. Mr. Darke has as yet only a few rough and highly-approximate measurements with provisional apparatus, but it has interested us very greatly to find that the amount of electric endosmosis which is observed, taken in conjunction with the results of the conductivity measurements, might indicate that potassium ion is hydrated in $\frac{N}{50}$

solution to the extent of about a dozen molecules of water on each ion of potassium. This is just about the degree of hydration which is required to correct the existing classical dissociation theory into a quantitative hydrate form of that theory, which is desirable in order to remove some of its outstanding difficulties such as, for example, the apparent deviations of electrolytes from the mass law.

Mr. A. S. E. Ackermann wrote that for the last three years he had been engaged on an investigation into the physical properties of London clay, which, owing to its being taken from just below the surface soil, was of yellow colour. One particularly interesting result which the experiments had brought out was the phenomenon which he has called the pressure of fluidity, which was got out by the following experiment.

A vertical guide and load-rod, with the equivalent of a ball and socket joint at its upper end, had fixed to its lower end, rigidly and at right angles to the rod, various-sized duralumin discs, one at a time. The disc was placed on the surface of well-puddled clay in a container, the clay containing a known percentage of water. Loads were applied to the top end of the guide-rod, and owing to the ball and socket arrangement the resultant of these loads was co-axial with the axis of the guide-rod. Measurements of the penetration produced by each increment of load were taken, and each load was allowed to act for 10 minutes before the measurement of penetration was recorded and a fresh increment of load added. The curves of these experiments (each dealing with either a different-sized disc or the same disc in clay containing a different percentage of water) were plotted, with the loads as ordinates and penetrations as abscissæ, and are roughly the quadrant of a circle, and then when a certain stress is reached the clay seems suddenly to break down, and the penetration continues apparently indefinitely at a constant speed without additional load until the disc is stopped from further motion by the bottom of the container. Roughly, during the early part of each experiment, the speed of penetration is about 1 mm. per minute; when the pressure of fluidity is reached, the speed becomes 1 cm. per minute. On making three experiments, in particular, with clay containing 29 per cent. of water, and using discs 26 mm., 37 mm. and 63 mm. in diameter, the same phenomenon was discovered in each case, and when the loads were divided by the areas of the respective discs the mean stress under the disc was 597 grms. per sq. cm.

Mr. Ackermann stated that he had never failed to obtain the pressure of fluidity, except in one case, where the clay contained only 17.5 per cent. of water, and was then so hard that, in spite of the stress being 11,540 grms. sq. cm. (= 10.5 tons/sq. foot), the penetration of the disc was only 5 mms., and there was no means of further increasing the stress. Two other experimenters have since repeated the experiment, and found the same effect in the same conditions. These are P. M. Crosthwaite, who also used London clay, and Lt.-Col. H. R. Lordly, who used some yellow clay obtained in Ithaca, New York, U.S.A.

As far as the experiments have gone, it has been found that the pressure of fluidity increases very rapidly as the water content decreases. If the experiments be plotted with the pressure of fluidity in kilos per sq. cm. as ordinates, and the percentage of water in the clay as abscissæ, then the drier end of the curve (that is, for clays containing between $25\frac{1}{2}$ per cent. and 22 per cent. of water) is a straight line, the equation to which is $p' = 39.5 - 1.48 w'$, where p' is the intensity of pressure under the disc in kilos per sq. cm. and w' is the percentage of water content. Between $25\frac{1}{2}$ per cent. and 38 per cent. of water, the experimental results agree more closely with the curve, the equation to which is $p' = \frac{1,073 \times 10^{10}}{(w')^7}$

It is considered that this pressure of fluidity is of importance in connection with land slides (where there is a low-lying layer of clay), cuttings, foundations of all kinds, retaining walls, piles and that it is probably closely associated with the viscosity of the clay when it is thus acting like a fluid. The experiments have shown that a general pressure on the *whole* mass of clay does *not* render it fluid-like; only when a portion is loaded does the phenomenon occur.

APPENDIX I

THE PROTEINS AND COLLOID CHEMISTRY*

BY

JACQUES LOEB,

THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH

I

The proteins, like certain other constituents of protoplasm, are colloidal in character, *i.e.* they are not able to diffuse through animal membranes which are permeable to crystalloids. For this reason a number of authors have tried to explain the behaviour of proteins from the view-point of the newer concepts of colloid chemistry. Foremost among these concepts is the idea that the reactions between colloids and other bodies are not determined by the purely chemical forces of primary or secondary valency, but follow the rules of "adsorption." Although a number of authors, during the last 20 years, *e.g.*, Bugarszky and Liebermann, Hardy, Pauli, Robertson, Sørensen, and others, have advocated a chemical conception of the reactions of proteins, their experiments failed to convince the other side, since these experiments could just as well be explained on the basis of the adsorption theory. There were two reasons for this failure. First, the experiments did not show that ions combined with proteins in the typical ratio in which the same ions combine with crystalloids. This proof only became possible when it was recognised that the hydrogen ion concentration of the protein solution determines the amount of ion entering into combination with a protein, and that therefore the ratios in which different ions combine with proteins must be compared for the same hydrogen ion concentrations. Since the former workers were in the habit of comparing the effects of the same quantities of acid or alkali added instead of comparing the behaviour of proteins at the same hydrogen ion concentration, they were not able to furnish the final proof for the purely chemical character of the combinations between ions and proteins, and nothing prevented chemists from assuming that proteins formed only adsorption compounds with acids, bases and neutral salts.

The second reason for the failure to prove the purely chemical character of the protein compounds lay in the so-called Hofmeister series of ion effects. Hofmeister was the first to investigate the effects of different salts on the physical properties of proteins, and he and his followers observed that the relative effect of anions on the precipitation, the swelling and other properties of proteins was

* The writer's experiments, on which this address is based, have appeared in the *J. Gen. Physiol.*, 1918-19, i, 39, 237 363, 483, 559; 1919-20, ii, 87; 1920-21, iii, 85, 247. 391.

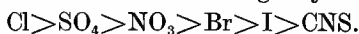
very definite, and that the anions could be arranged in definite series according to their relative efficiency, the order being independent of the nature of the cation. Similar series were also found for the cations, though these series seemed to be less definite. These Hofmeister series were a puzzle, inasmuch as it was impossible to discover in them any relation to the typical combining ratios of the ions, and this lack of chemical character in the Hofmeister series induced chemists to explain these series on the assumption of a selective adsorption of these ions by the colloids.

To illustrate this, we will quote the order which, according to Pauli, represents the relative efficiency of different acids on the viscosity of blood albumin—



where HCl increased the viscosity most and trichloroacetic or sulfuric least. In this series the strong monobasic acid HCl is followed by the weak monochloroacetic acid, this is followed by the dibasic oxalic acid; later follows a weak tribasic citric acid, then the very weak monobasic acetic acid, then the strong dibasic sulfuric acid, and finally again a monobasic acid, trichloroacetic. Pauli is a believer in the chemical theory of the behaviour of proteins, but it is impossible to harmonize his series of anions with any purely chemical theory of the behaviour of proteins.

The ion series of Hofmeister are no more favourable for a chemical conception. Thus, according to Hofmeister, gelatin swells more in chlorides, bromides and nitrates than in water, while in acetates, tartrates, citrates or sugar it swells less than in water. R. Lillie arranges ions according to their depressing effect on the osmotic pressure of gelatin solution in the following way—



These series again betray no relation to the stoichiometrical properties of the ions. As long as these Hofmeister ion series were believed to have a real existence it seemed futile to decide for or against a purely chemical theory of the behaviour of proteins since even with a bias in favour of a chemical theory the ion series remained a puzzle.

The writer believes to have removed these difficulties by using protein solutions of the same hydrogen ion concentration as the standard of comparison. In this way he was able to show that acids, alkalies and neutral salts combine with proteins by the same chemical forces of primary valency by which they combine with crystalloids, and that, moreover, the influence of the different ions upon the physical properties of proteins can be predicted from the general combining ratios of these ions. The so-called Hofmeister series have no real existence, being the result of the fact that the older workers failed to measure the most important variable in the case, namely, the hydrogen ion concentration of their protein solutions, a failure for which they cannot be blamed since the methods were not sufficiently developed.

II

Pauli and a number of other workers assume that both ions of a neutral salt are adsorbed simultaneously by non-ionised protein molecules. If we consider the hydrogen ion concentration of the proteins we can show that only the cation or only the anion or that

neither ion can combine at one time with a protein; and that it depends solely on the hydrogen ion concentration of the solution which of the three possibilities exists.

Proteins exist in three states, defined by their hydrogen ion concentration, namely: (a) as non-ionogenic or isoelectric protein, (b) as metal proteinate (*e.g.*, Na or Ca proteinate), and (c) as protein-acid salts (*e.g.*, protein chloride, protein sulfate, &c.). We will use gelatin as an illustration. At one definite hydrogen ion concentration, namely, $10^{-4.7}$ N (or in Sørensen's logarithmic symbol at $pH = 4.7$), gelatin can combine practically with neither anion nor cation of an electrolyte. At a $pH > 4.7$ it can combine only with cations (forming metal gelatinates, *e.g.* Na gelatinates), at a $pH < 4.7$ it combines with anions (forming gelatin chloride, &c.). This was proved in the following way:—Doses of 1 gm. of finely powdered commercial gelatin (going through sieve 60, but not through 80), which happened to have a pH of 7.0, were brought to a different hydrogen ion concentration by putting them for 1 hour at about 15° C. into 100 c.c. of HNO_3 solutions varying in concentration from M/8192 to M/8. After this they were put on a filter, the acid being allowed to drain off, and were washed once or twice with 25 cc. of cold water (of 5° C. or less) to remove remnants of the acid between the granules of the powdered gelatin. These different doses of 1 gm. of gelatin, now possessing a different pH , were all put for 1 hour into beakers containing the same concentration, *e.g.* M/64, of silver nitrate at a temperature of 15° C. They were then put on a filter and washed six or eight times each with 25 c.c. of ice-cold water; the wash water must be cold, since otherwise the particles will coalesce and the washing will be incomplete. This washing serves the purpose of removing the $AgNO_3$ held in solution between the granules, thus allowing us to ascertain where the Ag is in combination with gelatin and where it is not in combination, since the Ag not in combination with gelatin can be removed by the washing while the former cannot (or at least only extremely slowly by altering the pH). After having removed the $AgNO_3$ not in combination with gelatin by washing with ice-cold water, we melt the gelatin by heating to 40° C., adding enough distilled water to bring the volume of each gelatin solution to 100 c.c., determine the pH of each solution potentiometrically or colorimetrically, and expose the solutions in test-tubes to light, the previous manipulations having been carried out in a dark room (with the exception of the determination of pH , for which only part of the gelatin solution was used). In 20 minutes all the gelatin solutions with a $pH > 4.7$, *i.e.* from pH 4.8 and above, become opaque and then black, while all the solutions of $pH < 4.7$, *i.e.* from 4.6 and below, remain transparent even when exposed to light for months or years. The solutions of pH 4.7 become opaque, but remain white, no matter how long they may have been exposed to light. At this pH —the isoelectric point—gelatin is not in combination with Ag, but it is insoluble. Hence the cation Ag is only in chemical combination with gelatin when the pH is > 4.7 . At pH 4.7 or below gelatin is not able to combine with Ag ionogenically. This statement was confirmed by volumetric analysis.

The same tests can be made for any other cation the presence of which can be easily demonstrated. Thus when powdered gelatin of different pH is treated with $NiCl_2$ and the $NiCl_2$ not in combination with gelatin be removed by washing with ice-cold water, the presence of Ni can be demonstrated in all gelatin solutions with a $pH > 4.7$

by using dimethylglyoxime as an indicator. All gelatin solutions of pH of 4.8 or above assume a crimson colour upon the addition of dimethylglyoxime, while all the others remain colorless. When we treat gelatin with copper acetate, and wash afterwards, the gelatin is blue and opaque when its pH is 4.8 or above, but is colorless and clear for $pH < 4.7$. Most striking are the results with basic dyes, *e.g.*, basic fuchsin or neutral red, after sufficient washing with cold water; only those gelatin solutions are red whose pH is above 4.7, while the others are colorless.

On the acid side of the isoelectric point, *i.e.* at $pH < 4.7$, the gelatin is in combination with the anion of the salt used. This can be demonstrated in the same way by bringing different doses of powdered gelatin to different pH and treating them for 1 hour with a weak solution of a salt whose anion easily betrays itself, *e.g.* $M/128 K_4Fe(CN)_6$. If, after this treatment, the powdered gelatin is washed six times with cold water to remove the $Fe(CN)_6$ not in chemical combination with gelatin, and if 1 per cent. solutions of these different samples of gelatin are made, it is found that when the pH is < 4.7 the gelatin solution turns blue after a few days (due to the formation of ferric salt), while solutions of gelatin with a pH of 4.7 or above remain permanently colorless. Hence gelatin enters into chemical combination with the anion $Fe(CN)_6$ only when the pH is < 4.7 . The same can be demonstrated through the addition of ferric salt when gelatin has been treated with $NaCNS$, the anion CNS being in combination with gelatin only where the pH is < 4.7 . Acid dyes, like acid fuchsin, combine with gelatin only when the pH is < 4.7 .

In this way it can be shown that when the pH is > 4.7 gelatin can combine only with cations; when the pH is < 4.7 it can combine only with anions, while at pH 4.7 (the isoelectric point) it can combine with neither anion nor cation. The idea that both ions influence a protein simultaneously is no longer tenable.

It follows also that a protein solution is not adequately defined by its concentration of protein, but that the hydrogen ion concentration must also be known since each protein occurs in three different forms—possibly isomers—according to its hydrogen ion concentration.

In the experiments just discussed it was necessary to wash the powdered gelatin to find out at which pH an ion was in combination with the gelatin. This has led some authors to the belief that in all my experiments the washing was a necessary part of the procedure. I therefore will call especial attention to the fact that the experiments to be described in the rest of the paper were carried out with isoelectric gelatin to which just enough acid or alkali was added to bring it to the hydrogen ion concentration required for the purpose of the experiment.

III

When a protein is in a salt solution, *e.g.* $NaCl$, it will combine with Na forming sodium proteinate as soon as the pH is higher than the isoelectric point of the protein; when, however, the pH falls below that of the isoelectric point of the protein the Na is given off and protein chloride is formed.

Moreover, the writer has been able to show by volumetric analysis that the quantity of anion or cation in combination with the protein is an unequivocal function of the pH . When we add HCl to isoelectric gelatin and determine the pH we always find the same amount of Cl

in combination with a given mass of originally isoelectric gelatin for the same pH ; so that if we know the pH and the concentration of originally isoelectric gelatin present, we can also tell how much Cl is in combination with the protein for this pH . The same is true when we add an alkali to the isoelectric gelatin. For the same pH the amount of cation in combination is always the same. These facts have led the writer to propose the following theory:—When we add an acid, *e.g.* HCl , to isoelectric gelatin (or any other isoelectric protein) an equilibrium is established between free HCl , protein chloride, and non-ionogenic or isoelectric protein, and when we add an alkali an equilibrium is established between metal proteinate, non-ionogenic or isoelectric protein, and the hydrogen ion concentration. Sørensen was led to a similar view on the basis of entirely different experiments.

IV

This fact that the hydrogen ion concentration of a protein solution determines the quantity of protein salt formed is the basis on which

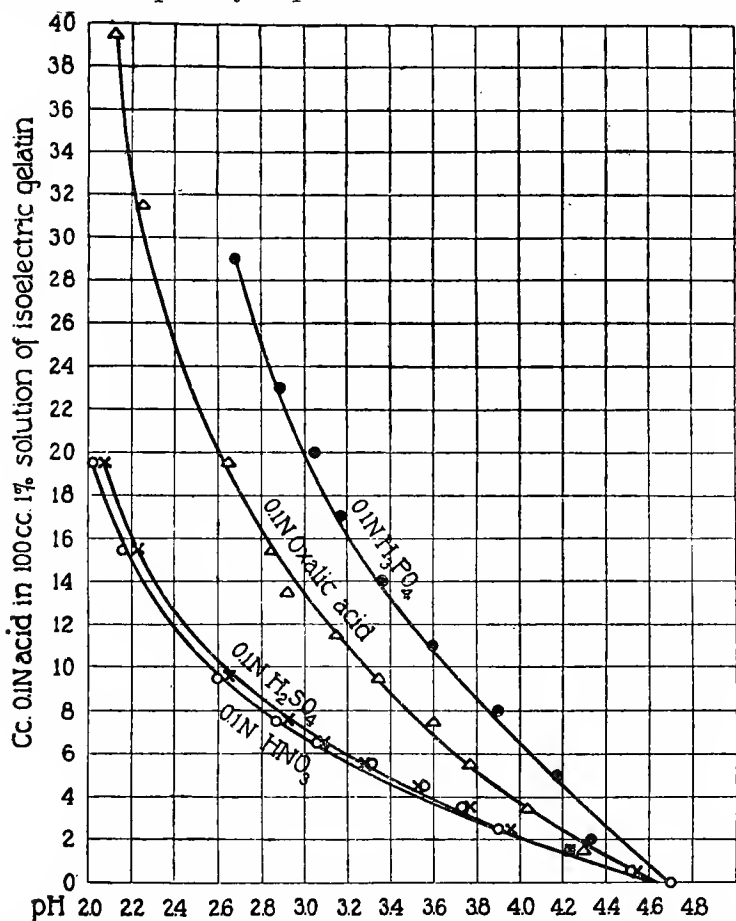


Fig. 1.—The ordinates represent the c.c. of 0.1 N acid in 100 c.c. of 1 per cent. solution of isoelectric gelatin required to bring the solution to the pH indicated in the abscissæ. The curves for 0.1 N, H_2SO_4 and 0.1 N, HNO_3 are identical, while the values for H_3PO_4 and oxalic acid differ, being approximately in the ratio of HNO_3 : oxalic acid : H_3PO_4 as 1 : 2 : 3.

the following proof for the purely chemical character of the combination between proteins and other bodies rests. The experiments mentioned thus far in this paper do not yet allow us to decide whether the ions are "adsorbed" or in chemical combination with the proteins. We will now show that acids and bases combine with proteins in the same way as they combine with crystalline compounds; namely, by the purely chemical forces of primary valency. The combination between acids and proteins is analogous to that between acids and NH_3 , and the combination between bases and proteins is analogous to that between CH_3COOH and an alkali. This can be proved in the following way:—We know that a weak dibasic or tribasic acid gives off one hydrogen ion more readily than both or all three; while in a strong dibasic acid, like H_2SO_4 , both hydrogen ions are held with a sufficiently small electrostatic force to be easily removed. If the forces which determine the reaction between these acids and proteins are purely chemical it would follow that three times as many c.c. of 0.1 N, H_3PO_4 are required to bring 100 c.c. of 1 per cent. solution of isoelectric gelatin to a given $p\text{H}$, *e.g.* 3.0, as are required in the case of HNO_3 or HCl ; while twice as many c.c. of 0.1 N oxalic as of HNO_3 should be required. On the other hand, it should require just as many c.c. of 0.1 N, H_2SO_4 as HNO_3 . Fig. 1 shows that this is the case. The ordinates of this figure are the c.c. of 0.1 N acid required to bring 1 gm. of isoelectric gelatin to the $p\text{H}$ indicated in the abscissæ by the four acids mentioned, namely, HNO_3 , H_2SO_4 , oxalic and phosphoric acids. The curves for H_2SO_4 and HNO_3 are identical, while, for the same $p\text{H}$, the value for H_3PO_4 is always approximately three times, and the value for oxalic acid is always approximately twice as high as for HNO_3 .

On the basis of the same reasoning as applied to acids we should expect that equal numbers of c.c. of 0.1 N, $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ as of LiOH , NaOH and KOH should be required to bring 100 c.c. of a 1 per cent. solution of isoelectric gelatin to the same $p\text{H}$, and the writer was able to show that this is the case. Similar results were obtained with crystalline egg albumin.

When we have a solution of a gelatin-acid salt of originally 1 per cent. isoelectric gelatin and of a certain $p\text{H}$, *e.g.* 3.0, we have free acid in the solution and a certain amount of the anion of the acid in combination with gelatin. We can find out by volumetric analysis how much of the anion is in combination with the protein by making certain corrections discussed in former papers. In this way it can also be ascertained that all weak dibasic acids combine in molecular proportions with isoelectric protein, while strong dibasic acids and diacidic alkalies combine in equivalent proportions with proteins, as is shown by Table I. It follows from this table that for the same $p\text{H}$ the amount of HNO_3 , oxalic and phosphoric acids in combination with the same quantity of originally isoelectric gelatin is always in the proportion of 1 : 2 : 3.

TABLE I

C.c. of 0.01 N acid in combination with 10 c.c. of a 1 per cent. gelatin solution at different pH.

$p\text{H}$.	3.1	3.2	3.3	3.4	3.5	3.7	3.9	4.1	4.2	4.3
HNO_3	4.35	4.1	3.6	3.2	2.85	2.45	1.9	1.45		0.75
Oxalic acid.	9.6	8.75	7.6	6.7	6.00	4.3	3.0		1.65	
H_3PO_4	-	12.4	10.4	9.8	9.00	7.4	5.8	4.5	2.6	2.1

We can, therefore, state that the ratios in which ions combine with proteins are identical with the ratios in which the same ions combine with crystalloids. Or, in other words, the forces by which gelatin and egg albumin (and probably proteins in general) combine with acids or alkalis are the purely chemical forces of primary valency.

V

The most important fact for our purpose is that from the combining ratios just mentioned the influence of acids and bases on the physical properties of proteins can be predicted. This influence is altogether different from that stated in the so-called Hofmeister series of ions or by the ion series of Pauli and his collaborators, and this difference is due to the fact that these latter authors compared the effects of equal quantities of acids or alkalis while we found it necessary to compare the physical properties of solutions of proteins of the same hydrogen ion concentration. If this is done the following rule is found:—All those acids whose anion combines as a monovalent ion raise the osmotic pressure, viscosity, swelling of protein about twice as much as the acids whose anion combines as a bivalent anion for the same pH. The same valency rule holds also for the cations of different alkalis.

We have seen that at the same pH three times as many c.c. of

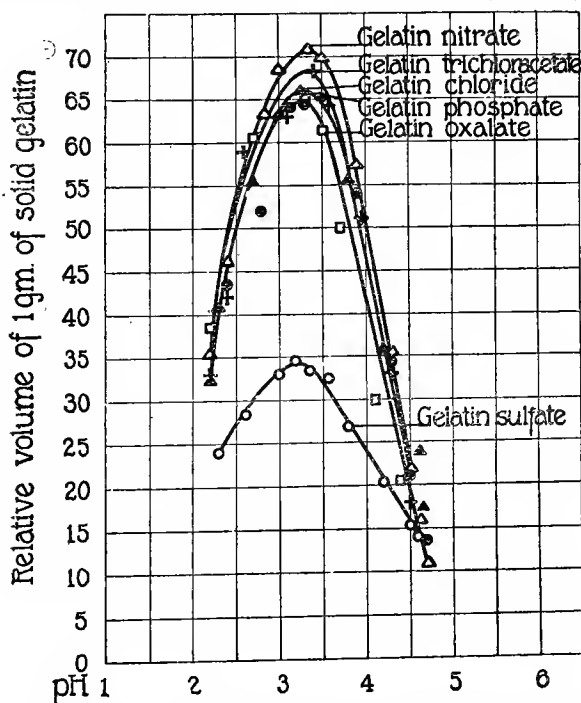


Fig. 2.—Influence of different acids upon the swelling of gelatin when plotted over pH as abscissæ. The curves show that nitric, trichloracetic, hydrochloric, phosphoric, oxalic and citric acids cause approximately the same degree of swelling, while sulfuric acid causes only about one-half the amount of swelling. In the case of gelatin sulfate the anion is divalent; in the case of the other acids used it is monovalent. According to the Hofmeister series the curves for phosphate, oxalate and citrate should coincide with that of sulfate, instead of coinciding with that of chloride.

0.1 N, H_3PO_4 as of HNO_3 are in combination with 1 gm. of originally isoelectric gelatin in 100 cc. of solution. It follows from this that the anion of gelatin phosphate is the monovalent ion H_2PO_4 and not the trivalent anion PO_4 . It follows likewise from the combining ratios discussed that the anion of oxalic acid in combination with protein is the monovalent anion HC_2O_4 . The same is true for all weak dibasic or tribasic acids, namely, that they combine with proteins forming protein salts with monovalent anion. It follows also from the combining ratios that the salt of a protein with a strong dibasic acid, as H_2SO_4 , however, must have a divalent anion, *e.g.* SO_4 . If we compare the viscosity or osmotic pressure of 1 per cent. solutions of originally isoelectric gelatin with different acids of the same pH, we find that these properties are identical for all gelatin salts with monovalent anion; in other words, 1 per cent. solutions of gelatin chloride, bromide, nitrate, tartrate, succinate, citrate or phosphate have all the same viscosity, and the same osmotic pressure at the same pH. The same is true for the swelling (Fig. 2). If we plot the curves for these three properties with pH as abscissæ and the values for osmotic pressure, viscosity and swelling as ordinates, we get practically identical curves for gelatin chloride, bromide, nitrate, tartrate, succinate, citrate and phosphate. The values for swelling are a minimum at pH 4.7 (the isoelectric point of gelatin), they rise rapidly with the fall of pH until they reach a maximum at pH about 3.2, and then they drop again. Each curve is the expression of an individual experiment. The maximum in the curves for gelatin chloride, bromide, nitrate, tartrate, succinate, citrate, and phosphate is practically identical, the variations between the values for these acids lying within the limit of variation which we may expect if we plot six different experiments with the same acid. When, however, we plot the same curves for gelatin sulfate, we get curves which are considerably lower, reaching a height of only one-half (or a little less) than those of gelatin-acid salts with monovalent anions. It may be of interest to compare our curves with those expected on the basis of Pauli's and Hofmeister's ion series. According to the latter theory the curves for phosphates, oxalates, citrates and tartrates should be in the region of the SO_4 curve, but not in the region of the Cl curve. Those authors who observed such differences did not measure the hydrogen ion concentration, attributing the effects due to the difference in the hydrogen ion concentration of their gelatin solutions erroneously to a difference in the anion effect. These elementary errors form the basis of a number of speculations current in biology and pathology.

When we compare monobasic acids of different strength, *e.g.* acetic, mono-, di-, and trichloroacetic acids, we find that the weaker the acid the more acid must be contained in a 1 per cent. solution of originally isoelectric gelatin to bring it to the same pH. If we compare the effect of these four acids on the osmotic pressure of gelatin we find that it is (within the limits of accuracy of these experiments) identical for the same pH. The curves for the influence of these four acids on the osmotic pressure of gelatin solution are practically identical when plotted over the pH as abscissæ; and, moreover, the curves are identical with the curves for HCl or H_3PO_4 in Fig. 1. The explanation of this fact is that at the same pH the same mass of originally isoelectric gelatin is in combination with the same quantity of these four acids, and since the anions of these four acids are all monovalent the curves must be identical.

As far as the alkalies are concerned, we notice that the curve representing the effect of the weak base NH_4OH on the physical properties of proteins is the same as that for the strong bases LiOH , NaOH , KOH when plotted over $p\text{H}$ as abscissæ, while the curves representing the effect of $\text{Ca}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$ on the same properties are considerably lower.

It is obvious that the valency of the ion in combination with the protein has a noticeable influence on the properties of the protein salt formed, while the protein salts with ions of the same valency have all the same properties. The fact of the greatest importance is, however, that the influence of acids and bases on the physical properties of proteins is the expression of the combining ratios of the acids or bases with proteins so that we are able to predict the value of these physical properties from the combining ratios. This fact seems to give a final decision in favour of a purely chemical theory of these influences and against the colloidal theories as based on the Hofmeister or Pauli ion series.

The behaviour of the proteins therefore contradicts the idea that the chemistry of colloids differs from the chemistry of crystalloids.

APPENDIX II

ON THE INTERNAL PRESSURE OF LIQUIDS

BY

H. KNEEBONE TOMPKINS, D.Sc.

This paper was written in 1896 as an Inaugural Dissertation for the Degree of Doctor of Science of the University of London. As it has never been published, the Joint Committee which organised the General Discussion is of opinion that the present Report affords a suitable opportunity for publishing the results of an investigation of historical importance by a very early and accurate worker in the field of colloidal physics.

ON THE INTERNAL PRESSURE OF LIQUIDS

BY

H. KNEEBONE TOMPKINS, D.Sc.

MANY attempts have been made to determine osmotic pressures and rates of diffusion by means of colloidal septa, but the results have generally been very complex, partly on account of the change of molecular aggregation which takes place with change of concentration in aqueous solutions, and partly because swollen colloids are rarely perfectly impervious to the diffusing substances. No examination, so far as I am aware, has been made of the expansion of the colloid itself when placed in a liquid in which it can swell, or of any change of volume which the swollen colloid may experience when submitted to the action of saline solutions. It seemed to me probable that the swelling of colloids might be due to osmotic pressure, and that in the swollen colloid we might have a substance sensitive to such pressures.

For the purpose of the investigation the ordinary colloids such as gelatin, agar-agar, &c., which swell in water, were discarded owing to the above-mentioned complexity, and use was made of a peculiar property of indiarubber.

If pure caoutchouc be placed in carbon bisulphide it swells up considerably and eventually dissolves, forming a thick viscous liquid. Vulcanised indiarubber, on the other hand, behaves quite differently. It swells rapidly at first, afterwards more and more slowly, but preserves its original form, and after about five hours reaches its maximum volume, which in the case of black rubber-tubing is six to seven times that which it originally possessed. The matter extracted by the carbon bisulphide consists mainly of uncombined sulphur, the amount of rubber dissolved being not greater than one per cent. of the substance taken. The indiarubber in its expanded state preserves a good deal of its original elasticity, and if exposed to the air gradually contracts to its original volume and is to all appearance completely unaltered. It seemed probable that the expanded rubber would be sensitive to the osmotic pressure of substances added to the carbon bisulphide, and this has proved to be the case.

The proposed method of experiment consisted in placing a piece of vulcanised rubber in carbon bisulphide until it had reached its maximum volume, which was to be determined by some suitable means, and then dissolving in the carbon bisulphide a given proportion of some other substance and noting any further increase or decrease of volume.

General Properties of Indiarubber.—The material used for these experiments was ordinary black indiarubber tubing of $\frac{1}{4}$ inch external diameter. It was cut into lengths of one inch and was extracted two or three times with carbon bisulphide in order to remove uncombined sulphur, as it was thought that the latter might influence the results by its osmotic pressure. The rubber was then exposed to the air until thoroughly free from carbon bisulphide.

Specific Gravity.—This value is very constant for the same sample of tubing. The following are six determinations taken at random :—

1 grm. of rubber =	1.0638 c.c.
	1.0640
	1.0684
	1.0655
	1.0623
	1.0689

Maximum Expansion of Rubber in Carbon Bisulphide.—A weighed piece of indiarubber tubing was placed in carbon bisulphide until thoroughly expanded. It was then hooked out on a piece of bent wire, and quickly dropped into a weighing-tube which had been lined with filter-paper. The stopper was at once inserted, and the tube rolled round in order to remove carbon bisulphide adhering to the rubber. The tube was then opened for a moment and the paper removed with the balance-tongs. The whole was then weighed. From the increase in weight of the rubber the volume of the absorbed carbon bisulphide can be calculated, if the specific gravity of the latter at the temperature of the experiment is known; and this volume added to the volume of the piece of rubber taken will give the total volume of the rubber when expanded, on the assumption that the volume of the expanded rubber is made up of the volume of the original rubber and that of the absorbed carbon bisulphide (Method B).

As a check to this result the weighing-tube was next opened and filled up with recently boiled water (if ordinary water is used the rubber soon becomes coated with air-bells), the stopper carefully inserted, and the whole weighed. In this way a direct determination of the volume of the expanded rubber is effected (Method A). The weighing-bottle had a well-fitting stopper in which a groove was filed to allow the excess of water to escape, and it was always inserted in the same position and with approximately the same pressure. The bottle was carefully calibrated, and it was found that consecutive weighings when full of water did not differ by more than .005 gm. The pieces of rubber taken weighed about .7 gm. The following results were obtained:—

Maximum Volume calculated on 1 c.c. of Rubber

			Method A.	Method B.
Piece 1	-	-	6.8788 c.c.	6.8885 c.c.
2	-	-	6.8085	6.8178
3	-	-	6.8037	6.8157
4	-	-	6.6622	6.6601
5	-	-	7.5605	7.5563
6	-	-	7.4982	7.4948
7	-	-	7.7373	7.7385
8	-	-	6.7616	6.7695

It will be seen from these results that the two methods of measuring the expansion give closely agreeing results with the same piece of rubber, and are therefore reliable methods of measurement, but that the volume attained by different pieces of rubber from the same piece of tubing are widely different, probably owing to variation in the extent to which the rubber has been vulcanised. It is therefore evident that any change of volume of the expanded rubber due to the osmotic pressure of substances subsequently added to the carbon bisulphide would not be comparable if different pieces of rubber were used.

Experiments were next made to see if the same piece of rubber could be used consecutively, or whether the elasticity changed each time it was expanded with carbon bisulphide. For the purpose a piece of tubing was placed in carbon bisulphide until expanded, and the expansion was then determined by Method B. It was then suspended in air and left until the carbon bisulphide had completely evaporated, again placed in carbon bisulphide, and the expansion determined, and so on.

Weight of rubber	-	.7385 gm.
Volume (cal. on 1 c.c.) after 1st treatment with CS ₂		6.7616 cc.
" " " 2nd "		6.8054
" " " 3rd "		6.8657
" " " 4th "		6.9685
Weight of rubber after the four treatments	-	.7165 gm.

It is evident that the volume elasticity of the rubber is not constant, even for the same piece, but decreases at each treatment with carbon

bisulphide; a result which is doubtless due to the slow solvent effect of the carbon bisulphide, the rubber having lost 2.9 per cent. during the four treatments.

In order to make sure that the expansion of the rubber had practically ceased at the end of the time allowed for each experiment (24 hours), a sample was left in carbon bisulphide and weighed from day to day. The following are the results:—

Volume (cal. on 1 c.c.) after 24 hours -	-	-	7.5293 c.c.
" " " 96 " -	-	-	7.5432

Another sample changed in volume from 7.6453 to 7.7365 in three weeks. The vulcanised rubber is therefore practically insoluble, at any rate in a limited quantity (12 c.c.) of carbon bisulphide.

Since the elasticity of the rubber is constant only whilst it remains distended, and since it cannot be again brought to the same condition in a second experiment, some means was sought of expressing the results so that they might be comparable. The equation for volume elasticity is

$P = k \frac{v}{V}$, where P is the pressure causing change of volume, V the initial volume of the body, and v the change of volume under the influence of the pressure; and it was thought that if the change of volume produced by diffusing substances was expressed in terms of the original volume of the expanded rubber, the results would be comparable for small values of " v " even if the size and elasticity of the pieces of rubber varied. The nature of the curves obtained have borne out this conclusion.

Method of Experiment.—Several methods of determining change of volume of rubber under the influence of osmotic pressure were tried. The following appeared the most satisfactory. A piece of $\frac{1}{4}$ -inch tubing 1 inch long is weighed and its volume calculated from the specific gravity of the sample. It is then placed in a weighed corked test-tube, 12 c.c. of carbon bisulphide are added, and the rubber is left for 24 hours to expand. At the end of this time it is hooked out and its volume is determined by Method B. The rubber is then returned to the test-tube, and the whole is weighed. The weight less that of the test-tube and original rubber gives the weight of the carbon bisulphide. A small proportion (0.5 cc., for instance) of the substance whose osmotic pressure is to be measured is next added, and the whole again weighed. The liquid is well mixed and the rubber left in it for 24 hours to undergo any further change of volume due to the osmotic pressure of the added substance. It is then removed, and its volume and specific gravity determined by means of Method A. From its specific gravity the proportion of the added substance within the rubber can be calculated, and this deducted from the total amount taken gives the proportion of substance in the liquid outside the rubber. An example in which acetone was the substance under examination will serve to make the method clearer.

Data

Weight of rubber -	-	-	-	-	-	-	6190
Wt. of test-tube + rubber -	-	-	-	-	-	-	9.7540
Wt. of rubber (expanded with CS ₂) + w.-tube (1)	-	-	-	-	-	-	16.7600
" " " " " (2)	-	-	-	-	-	-	16.7610
Wt. of test-tube + rubber + CS ₂ -	-	-	-	-	-	-	24.6400
" " " " + acetone (0.5 c.c.) -	-	-	-	-	-	-	25.0650
Wt. of rubber (expanded with CS ₂ + acetone) (1)	-	-	-	-	-	-	16.8425
" " " " (2)	-	-	-	-	-	-	16.8360
" " in water -	-	-	-	-	-	-	30.6385
Wt. of weighing-tube -	-	-	-	-	-	-	11.3475
" " + water (14° C.) -	-	-	-	-	-	-	29.6930
Sp. gr. CS ₂ 10" -	-	-	-	-	-	-	1.2723
" acetone 10" -	-	-	-	-	-	-	.8024

Calculations

Wt. of rubber taken	-	-	-	-	-	-	·6190
Vol. „ (calc.)	-	-	-	-	-	-	·6602

(1) Expansion with CS₂ only :—

Wt. of w.-tube + expanded rubber	-	-	-	-	-	-	16·7610
							11·3475

5·4135
·6190

Wt. of absorbed CS ₂	-	-	-	-	-	-	4·7945
Vol. (calc.)	-	-	-	-	-	-	3·7686
							·6602

Vol. of expanded rubber	-	-	-	-	-	-	4·4288
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(2) Expansion with CS₂ + acetone :—

Wt. of tube + expanded rubber	-	-	-	-	-	-	16·8360
							11·3475

5·4885
29·6930

Vol. of expanded rubber	-	-	-	-	-	-	4·5430
							·6602

Vol. of CS ₂ + acetone in rubber	-	-	-	-	-	-	3·8828
---	---	---	---	---	---	---	--------

Wt. of expanded rubber	-	-	-	-	-	-	5·4885
							·6190

Wt. of CS ₂ + acetone in rubber	-	-	-	-	-	-	4·8695
--	---	---	---	---	---	---	--------

It is evident from the above calculations that the expanded rubber has changed in volume from 4·4288 c.c. to 4·5430 c.c. under the influence of the acetone. Of the latter a portion is within the rubber, the rest without. Let w and w' be the weights of acetone and carbon bisulphide respectively in the rubber, and d and d' their densities, then

$$w + w' = 4·8695,$$

$$\frac{w}{d} + \frac{w'}{d'} = 3·8828.$$

From these equations, wt. of acetone in rubber = ·1200,
whence grm.-mols. per c.c. of rubber = ·00046.

The composition of the fluid outside the expanded rubber is easily calculated as follows :—

							25·0650
							24·6400
Wt. of acetone taken	-	-	-	-	-	-	·4250
„ acetone in rubber	-	-	-	-	-	-	·1200
Wt. of acetone outside rubber	-	-	-	-	-	-	·3050
Vol. „ „	-	-	-	-	-	-	·3801

								24·6400
								9·7540
Wt. of CS ₂ taken	-	-	-	-	-	-	-	14·8860
„ CS ₂ in rubber	-	-	-	-	-	-	-	4·7495
Wt. of CS ₂ outside rubber	-	-	-	-	-	-	-	10·1365
Vol. „ „	-	-	-	-	-	-	-	7·9671
								·3801
Vol. of liquid outside rubber	-	-	-	-	-	-	-	8·3472
Grm.-mols. acetone per c.c. of fluid outside the expanded rubber	-	-	-	-	-	-	-	·00063

We find, then, from the above set of experiments, that a certain piece of rubber expands to a volume of 4·4288 c.c. when placed in carbon bisulphide only, but to a volume of 4·5430 c.c. when placed in a mixture of carbon bisulphide and acetone, there being ·00046 grm.-molecules of acetone per c.c. inside the rubber, and ·00063 grm.-mols. per c.c. outside. Now in order to make several such results comparable, the first volume is called 100. The second then becomes 102·58, and 2·58 per cent. is the expansion produced by the acetone under the given distribution.

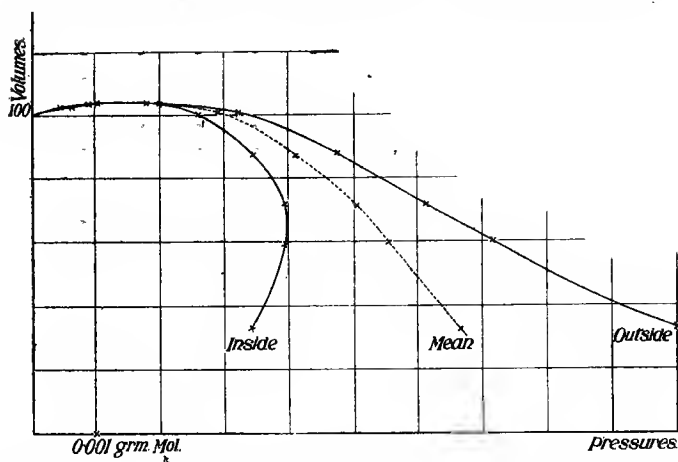
The chief difficulty in the experimental method on which the above results are based lies in getting the expanded rubber into the weighing-bottle in an exactly dry condition. If the rubber is exposed too much to the air in its passage from the test-tube there is a decided loss of carbon bisulphide and consequent contraction, whilst if it is dropped into the bottle in a distinctly wet condition, the filter-paper with which the latter is lined fails to remove the whole of the adhering fluid. With care consecutive weighings may be within ·01 grm. of one another. This would amount to an error of about 0·4 per cent. of the volume of the expanded rubber. As there are two determinations of volume for each set of results, the error may disappear or it may amount to 0·8 per cent. The calculations have been made on the assumption that there is no change of volume when organic liquids are mixed. This is probably approximately true when the proportion of one constituent is small (see later). I have already shown that the volume of rubber expanded with carbon bisulphide is made up of the volume of the original rubber plus that of the absorbed carbon bisulphide.

In the experiments substances were chosen whose specific gravities differed largely from that of carbon bisulphide, so that the composition of the fluid mixture within the rubber might be calculated with tolerable accuracy from its specific gravity. When now a series of experiments were made with gradually increasing quantities of acetone, the following results were obtained :—

Vol. of expanded rubber.	Grm.-mols. acetone inside.	Grm.-mols. acetone outside.
100	0	0
102·58	·00046	·00063
103·76	89	110
104·14	178	199
100·57	259	321
86·93	344	478
71·52	396	612
58·76	394	717
32·77	339	999

If these results are plotted so as to make the number of grm.-mols. per c.c. the abscissæ and the volumes the ordinates, two curves are obtained (Fig. 1) which nearly coincide at first but rapidly diverge as the volume of the rubber becomes less.

FIG. 1.—Acetone. Constituents per cc. Inside and Outside.



The peculiar shape of the curve representing the proportion of acetone inside the expanded rubber is evidently due to the fact that the relative space occupied by the rubber itself increases as the volume of the rubber decreases, hence there is less space for the fluid mixture within the rubber; moreover, as there is no affinity between the acetone and the rubber (acetone has little power *per se* to expand rubber) the former accumulates in the fluid outside. If the mean be taken between the two curves a new curve is obtained, the lower portion of which is a straight line, and which appears to be parabolic. It agrees well in its early part with the equation

$$p - ap^2 = kv,$$

where p is the mean number of grm.-mols. of acetone per c.c. inside and outside the rubber, v is the change of volume produced by the acetone, and a and k are constants. This is shown by the following calculated results:—

$$a = 333 \cdot 14.$$

$$k = \cdot 000172.$$

Grm.-mols. (mean)

per c.c.	Vol.	Do. cal.
·00054	102·58	—
99	103·76	103·86
188	104·14	104·08
290	100·57	—
411	86·93	91·20
504	71·52	80·15
555	58·76	72·67
669	32·77	47·68

This result is interesting in view of the recent work on the depression of the freezing point, &c. For with very small percentages of acetone the term ap^2 would disappear, and the equation would become $p = kv$; or the increase of volume is at first proportional to the amount of dissolved substance. Results to follow will show that it is proportional to the number of grm.-molecules, so that we have here an exact analogue of Raoult's well-known law. Next with regard to the term ap^2 , which becomes significant when larger quantities of acetone are present. Taking for granted that the change in volume of the rubber really represents the osmotic pressure of the dissolved substance, the expansion would at first be proportional to the number of molecules of acetone present, since the latter would at first exert a pressure equivalent to that of a perfect gas, but as the quantity of acetone increased the attraction between its molecules would become sensible and the pressure would begin to decrease.

The negative pressure due to the mutual attraction of the molecules of a gas varies according to van der Waals inversely as the square of the volume, that is directly as the square of the number of molecules in unit volume: hence the term ap^2 may be considered to represent the loss in pressure of the acetone due to the mutual attraction of its molecules.

Van der Waals' equation also involves the space $(V - b)$ surrounding the molecules of a gas. In the case of liquids, however, this is constant for the same liquid at the same temperature, and would remain so on dissolving the liquid in another one since the changes of volume on mixing organic liquids are so small as to be negligible. In fact, we may suppose that the molecules of a liquid are pressed so closely together that they do not readily undergo any further change, the molecular volumes of organic liquids calculated from their specific gravities being much smaller than the values calculated from " b " in van der Waals' formula. The force represented by " a " in the latter formula may, on the other hand, remain intact in mixed liquids, unless indeed the intervening liquid acts in some way as a dielectric, and we may therefore expect that the osmotic pressure will be represented by a quadratic expression. In giving the above interpretation to the equation $p - ap^2 = kv$, the change of volume of the expanded rubber has been supposed to be proportional to the total osmotic pressure of the dissolved substance, or, in other words, that the osmotic pressure of the dissolved substance is balanced by the volume-elasticity of the rubber. The equation for the latter is $P = k \frac{v}{V}$, but as in our case V is always 100, the equation becomes $P = Kv$.

It is now necessary to show that the equation for acetone is generally true for dissolved substances. The substance next taken was benzene, which differs from acetone in having a power of expanding rubber nearly equal to that of carbon bisulphide. The character of the curve, however, remains unaltered. The following are the results:—

Vol. of expanded rubber.	Grm.-mols. benzene, per c.c. inside.	Do. outside.
100	0	0
102.62	.00043	.00045
103.24	82	77
104.54	126	132
105.31	141	151
105.65	189	189
106.13	219	225
105.82	234	241
106.40	257	272
106.82	283	297
107.07	304	322
107.29	331	356

The values calculated for the equation $p - ap^2 = kv$ give the following results:—

$$a = 203.9.$$

$$k = .000205.$$

Grm.-mols. per c.c. (mean).	Vol.	Do. cal.
.00044	102.62	101.96
79	103.24	—
129	104.54	104.65
146	105.31	105.01
189	105.65	—
222	106.13	105.94
237	105.82	105.99
264	106.40	105.96
290	106.82	105.79
313	107.07	105.54
343	107.29	105.04

The first volume being undoubtedly erroneous the values for a and k have been calculated from points 2 and 5. The curve would terminate at a volume of 91.41 if continued far enough, this being the volume which rubber attains when placed in benzene alone. It lies, therefore, for the most part above the line of initial volume, and there is a much closer coincidence between the observed and calculated volumes than in the case of acetone. In other words, the attraction between the molecules of benzene is partially balanced by the attraction of the rubber for the benzene, the value for " a " is consequently much smaller, and the benzene behaves as a perfect gas for a greater distance along the curve. We may note here the interesting fact that a mixture of carbon bisulphide and benzene has a greater effect in expanding rubber than either constituent alone, the maximum volume with a mixture being about 107, whilst carbon bisulphide and benzene alone produce volumes of 100 and 91.41 respectively. The same thing is observed with chloroform and ether, which, like benzene, are soluble in rubber. This fact would seem to explain the superiority of mixed solvents over single ones in many cases, especially in the solution of resins, which are to some extent colloids. Colloidal solutions are always characterised by great viscosity, and it is doubtful if they are true solutions. Possibly the elasticity of a "soluble" colloid is so small that a balance between the osmotic pressure of the solvent and the elasticity is not easily reached, and the colloid therefore expands indefinitely.

Chloroform.—The following values were obtained :—

Vol.	Grm.-mols. per c.c. inside.	Do. outside.
102.55	.00025	.00068
104.29	50	110
106.30	96	169
108.52	159	244
109.54	190	269
111.06	217	313
111.21	241	328

Calculated values for the equation $p - ap^2 = kv$:—

$$a = 126.9.$$

$$k = .00017.$$

Grm.-mols. (mean)

per c.c.	Vol.	Co. cal.
.00046	102.55	—
80	104.29	104.23
132	106.30	106.46
201	108.52	108.81
228	109.54	—
265	111.06	110.35
284	111.21	110.69

The curve here is similar to that of benzene, and agrees well with the equation $p - ap^2 = kv$. The volume produced by chloroform alone is 112.9, hence the curve never dips below the line of initial volume.

Ether.—The following values were obtained :—

Vol.	Grm.-mols. per c.c. inside.	Do. outside.
102.23	.00037	.00037
103.58	62	68
104.75	95	107
105.47	117	134
106.83	146	167
107.83	165	192
107.94	189	219
107.73	205	239

Calculated values for the equation $p - ap^2 = kv$:—

$$a = 210 \cdot 13.$$

$$k = \cdot 000154.$$

Grm.-mols. per cc. (mean).	Vol.	Do. cal.
$\cdot 00037$	102.23	—
68	103.58	103.79
101	104.75	105.17
125	105.47	105.99
156	106.83	—
178	107.83	107.25
204	107.94	107.58
222	107.73	107.70

Two more substances were examined, namely, acetic ethyl ether and malonic ethyl ether. These substances, like acetone, have little power of expanding rubber by themselves, hence the curve soon reaches a maximum.

<i>Acetic Ether.</i>	Grm.-mols per c.c.	
Vol.	inside.	Do. outside.
102.19	$\cdot 00043$	$\cdot 00040$
103.72	79	71
105.44	203	205
105.16	233	252
101.14	300	336

Calculated values for the equation $p - ap^2 = kv$:—

$$a = 266 \cdot 3.$$

$$k = \cdot 000167.$$

Grm.-mols. per c.c. (mean.)	Vol.	Do. cal.
$\cdot 00041$	102.19	—
75	103.72	103.60
204	105.44	105.59
242	105.16	—
318	101.14	102.92

<i>Malonic Ether.</i>	Grm.-mols. per c.c.	
Vol.	inside.	Do. outside.
101.84	$\cdot 00064$	$\cdot 00038$
100.95	80	63
99.61	95	94
97.29	117	106
94.61	138	130

Values calculated for the equation $p - ap^2 = kv$:—

$$a = 1152.$$

$$k = \cdot 00011.$$

Grm.-mols. (mean) per c.c.	Vol.	Do. cal.
$\cdot 00051$	101.84	—
71	100.95	101.13
94	99.61	99.32
112	97.29	—
134	94.61	93.62

The observed volumes for these substances agree at first with those calculated, but soon diverge, as with acetone. The value for "a" is particularly large with malonic ether, as might be expected from its high boiling-point.

In measuring the osmotic pressures of the preceding seven substances, the initial state of the rubber has been its state when fully expanded with carbon bisulphide, it being assumed that the changes of volume were entirely due to the osmotic pressure of the dissolved substances, this pressure being eventually balanced by the volume-elasticity of the distended rubber; and that the carbon bisulphide simply served as a convenient vehicle for the introduction of the diffusing substance in a

molecular condition. In order to prove this a set of experiments were made in which the rubber was first distended with benzene. Small proportions of carbon bisulphide were then added, and any change of volume determined. The initial volume was in this case called 91.41, this being the volume produced by benzene alone when the volume produced by carbon bisulphide alone equals 100. The following results were obtained :—

Carbon bisulphide in Benzene.

Vol.	Grm.-mols. CS ₂ per c.c. inside.	Do. outside.
91.41	0.	0.
95.29	.00063	.00081
96.70	103	130
98.22	144	182
99.51	191	237

Values calculated for equation $p - ap^2 = kv$:—

Grm.-mols. (mean).	Vol.	Do. cal.
$a = 180.3.$		$k = .00016.$
.00072	95.29	—
116	96.70	97.06
163	98.22	98.50
214	99.51	

It will be seen that the observed values agree well with the equation $p - ap^2 = kv$. The values for a and k are also comparable with those obtained for the previous substances. Since the initial volume of the rubber is here 91.41 whilst in the previous sets of experiments it was 100, these results show that the swollen rubber really obeys the law for volume elasticity, at any rate for small (10 per cent.) charges of volume. I hope to examine this matter more fully.

Values for "a."—In explaining the equation $p - ap^2 = kv$ I have supposed " a " to represent the same value as it does in van der Waals' equation for gases, and it might at first be expected that it would be identical with it. It is found, however, that all liquids, except perhaps alcohol,* have a slight power of their own of diffusing into and expanding rubber, hence we must suppose that there is a slight attraction between the rubber and the molecules of the substance. The effect of such an attraction would be to spread the substance evenly throughout the rubber, and this force of attraction may therefore be supposed to act from within outwards and to oppose the mutual attraction of the molecules of the dissolved substance. The equation now becomes

$$p - (a - A)p^2 = kv$$

where " a " is van der Waals' value, and A the force of attraction between the rubber and the substance. This view is supported by the fact that all the substances examined conform to the expression $p - ap^2 = kv$ whether their solubility in rubber is great or small, and also that the divergence of the value " a " from van der Waals' value becomes greater as the solubility of the substance in rubber increases. This is shown by the following table :—

Values for " a ."	From van der Waals' equation (cal. on 1 c.c.).	Observed.	Max. vol.
Acetone	611.0	333.1	16.9
Acetic ether . . .	778.8	266.3	22.7
Ether	725.1	210.1	54.4
Benzene	980.2	203.9	91.4
Chloroform	642.3	126.9	111.4
Carbon bisulphide (in benzene)	490.1	180.3	100.0

* Experiments with alcohol were vitiated owing to traces of moisture which it contained, and which caused it to separate in globules from the carbon bisulphide after some time.

The values for " a " in van der Waals' equation are taken from Ostwald's "Outlines of General Chemistry," p. 87. His values have been multiplied by 22380, as in these experiments the unit of volume has been 1 c.c. instead of 1 litre. The maximum volume mentioned is the volume attained by rubber when placed in the liquid alone, the volume attained by the same piece of rubber when placed in carbon bisulphide being called 100. This maximum volume represents the solubility of the substance in rubber, and is taken as a rough measure of the attraction between the rubber and the liquid.

Now it will be seen that the observed value for " a " is always less than van der Waals' value, as is required by our theory, and that the ratio between them is always greater, the greater the attraction between the rubber and the substance. This is more clearly shown in the following table:—

	Van der Waals' value.		Max.
	Observed value.	vol.	
Acetone	1.83	16.9	
Acetic ether	2.92	22.7	
Ether	3.45	54.4	
Benzene	4.81	91.4	
Chloroform	5.06	111.4	
Carbon bisulphide (in benzene)	2.71	100.0	

So that in explaining the value for " a ," I suppose the molecules to be acted upon by two opposing forces—their mutual attraction, which is alone considered in van der Waals' equation, and the attraction between them and the mass of the surrounding matter, in virtue of which they diffuse. The latter force is probably due to both the rubber and the carbon bisulphide in which the substance is dissolved. This view is supported by the last result in the above tables, in which the substance (carbon bisulphide) was dissolved in benzene. The ratio between the two values for " a " is not now in line with the others. The effect of the rubber on the value for " a " might be reduced to a minimum by using a very slightly vulcanised specimen. The initial volume of the rubber would then be very large, and as a consequence the mass of the rubber per unit volume would be very small. The divergence of " a " from van der Waals' value would then be due entirely to the affinity of the solvent for the dissolved substance. I hope to make experiments on this point. The values for " a " obtained in this way would probably be less than those of van der Waals.

Values for " k ."—The following are these values for the substances examined:—

Chloroform	0.000170
Benzene	205
Ether	154
Acetic ether	167
Acetone	172
Carbon bisulphide	162
Malonic ether	114

These values should probably be nearly identical except in the case of malonic ether. In order to get a close value for k , it will be necessary to make a number of determinations of its value at an early part of the curve and take the mean, since the experimental error is greatest when the expansions are small. According to van der Waals' equation the pressure of a gas is inversely as $(V - b)$, the empty space surrounding the molecule. This would be constant for the same liquid as already pointed out, but would vary with different liquids, would be greater the greater the molecular volume and would probably be nearly proportional to it. Hence, since the molecular volume of malonic ether is nearly double of that of the other substances, its osmotic pressure is only

one half. It must be confessed that this explanation is not very satisfactory, the more so as nothing analogous is met with in the laws regulating the depression of the freezing-point, &c. It may be noted that the initial distribution of the substance inside and outside the rubber is very unequal in the case of malonic ether.

Distribution of Diffusing Substances inside and outside the Colloid.—Hitherto we have considered the curve produced by taking the mean number of grm.-molecules per c.c inside and outside the colloid for the abscissæ and the volumes of the colloid for the ordinates, as it was found that the most regular curve was obtained in this way in the original experiment with acetone. Moreover, the two curves (Fig. 1) representing the distribution of acetone inside and outside the colloid would eventually coincide with the mean curve when the colloid is infinitely expanded, that is when the conditions inside and outside the colloid are identical. For this reason the mean curve was considered best to represent the osmotic properties of the substance under examination. In order to investigate the unequal distribution of the diffusing substance produced by the presence of the colloid, it was though best to make use of the above two curves instead of attempting to apply ordinary diffusion data, as the rate of expansion of rubber when placed in carbon bisulphide could not be made to conform to Fick's law (*see later*). If the curves in question be examined, it will be seen that they run alongside of the mean curve for a considerable distance and do not differ from it greatly in character; and it will be found that they agree closely at first with the equation $p - ap^2 = kv$, " a " and " k " being different for the "inside" and "outside" curve. This is best seen with those substances—ether, benzene, and chloroform—which are themselves soluble in rubber and whose curves lie mostly above the line of initial volume. The following are the results:—

Benzene.—Inside.

$\alpha = 191.8. \quad k = .00021$		
Grm.-mols. per c.c inside	Vol.	Do. cal.
.00043	102.62	101.85
82	103.24	—
126	104.54	104.46
141	105.31	104.82
189	105.65	—
219	106.13	105.95
234	105.82	106.04
257	106.40	106.11
283	106.82	106.07
304	107.07	105.94
331	107.29	105.67

Outside.

$\alpha = 215.2. \quad k = .000198$		
Grm.-mols. per c.c outside.	Vol.	Do. cal.
.00045	102.62	102.04
77	103.24	—
132	104.54	104.76
151	105.31	105.14
189	105.65	—
225	106.13	105.85
241	105.82	105.84
272	106.40	105.68
297	106.82	105.40
322	107.07	104.99
356	107.29	104.20

Chloroform.—Inside.

Grm.-mols. per c.c. inside.	Vol.	Do. cal.
·00025	102·55	—
50	104·29	104·19
96	106·30	106·80
159	108·52	—
190	109·54	108·60
217	111·06	108·24
241	111·21	107·58

$$a = 280\cdot8. \quad k = \cdot000103.$$

Outside.

Grm.-mols. per c.c. outside.	Vol.	Do. cal.
·00068	102·55	—
110	104·29	104·07
169	106·30	106·15
244	108·52	108·72
269	109·54	—
313	111·06	110·96
328	111·21	111·44

$$a = 26\cdot52. \quad k = \cdot00026.$$

Ether.—Inside.

Grm.-mols. per c.c. inside.	Vol.	Do. cal.
·00037	102·23	—
62	103·58	103·53
95	104·75	105·03
117	105·47	105·88
146	106·83	—
165	107·83	107·34
189	107·94	107·86
205	107·73	108·13

$$a = 187\cdot7. \quad k = \cdot000155.$$

Outside.

Grm.-mols. per c.c. outside.	Vol.	Do. cal.
·00037	102·23	—
68	103·58	103·77
107	104·75	105·32
134	105·47	106·13
167	106·83	—
192	107·83	107·15
219	107·94	107·29
239	107·73	107·25

$$a = 224\cdot4. \quad k = \cdot000153.$$

We can now calculate the distribution of the diffusing substance for any given volume; for let $p - ap = kv$ represent the relation between volume and grm.-mols. per c.c. inside the colloid, and $p' - a'p'^2 = k'v$ represent the relation outside the colloid; then

$$\frac{p - ap^2}{p' - a'p'^2} = \frac{k}{k'}.$$

Now when p and p'^2 are both very small the second terms vanish and the expression becomes

$$\frac{p}{p'} = \frac{k}{k'} = K.$$

This is Henry's law for gases.

In our arrangement we have benzene, &c., dissolved in carbon bisulphide for the gas, the difference in density between the two parts which causes the unequal distribution being brought about by the presence

of the swollen colloid. In the case of a gas dissolved in water, the difference in density is due to the different states (vapour and liquid) in which the solvent exists. This difference will cease in the former case when the colloid dissolves, and in the latter when the critical temperature is reached.

If the quantities of dissolved substance are larger, we have

$$\frac{p}{p'} = \frac{a'}{a} \cdot \frac{1 \pm \sqrt{4akv}}{1 \pm \sqrt{4a'k'v}};$$

or the distribution of the gases is no longer a constant ratio but becomes a function of the increase in volume of the solvent. The vapour tension of solutions of ammonia, &c., might perhaps be investigated by means of this equation, as also that of mixed liquids.

The difference in the values for a and a' is evidently due to the attraction of the colloid for the dissolved substance, or rather to the difference in attraction of the colloid on the one hand and the solvent on the other.

There are not sufficient data to explain the ratio $\frac{k}{k'}$. In the case of benzene and ether this ratio is equal to unity, and these two substances have molecular weights equal to that of the solvent (CS_2). It will be seen that the values of a and k for benzene are nearly equal to those of a' and k' respectively; hence the distribution remains constant, as required by the above formula. This is seen in the following table.

Benzine.—Ratio of grm.-mols. per c.c. inside and outside the colloid.

Vol.	Benzene inside.	Do. outside.	Ratio $\frac{\text{outside.}}{\text{inside.}}$
100	0.	0.	
102.62	0.00043	0.00045	1.05
103.24	82	77	0.94
104.54	126	132	1.04
105.31	141	151	1.06
105.65	189	189	1.00
106.13	219	225	1.03
105.82	234	241	1.03
106.40	257	272	1.06
106.82	283	297	1.05
107.07	304	322	1.06
107.29	331	356	1.07

Volume attained by Rubber when placed in single fluids.—These values have already been mentioned. They are easily obtained by placing rubber in carbon bisulphide for 24 hours and determining its volume by method B. The carbon bisulphide is then allowed to evaporate, and the rubber when quite dry is placed in the liquid under examination for 24 hours, and the volume calculated as before. Finally the rubber, after drying, is placed once more in carbon bisulphide and the volume attained again determined. The mean of the two volumes in carbon bisulphide is called 100, and the volume attained by the rubber when placed in the liquid under investigation is referred to this value. The following are the results:—

Carbon bisulphide	-	-	-	100.0
Acetone	-	-	-	16.9
Acetic ether	-	-	-	22.7
Ether	-	-	-	54.4
Benzene	-	-	-	91.4
Chloroform	-	-	-	111.4
Vol. of unswollen rubber (average)				13.3

Change of Volume on mixing Organic Liquids.—The calculations of the results in the preceding experiments have been made on the assumption that the change of volume on mixing organic liquids is negligible, at any

rate when the proportion of one constituent is small. To prove this, mixtures were made with weighed quantities of alcohol and carbon bisulphide, and the density of the mixture was determined. The number of grm.-molecules of alcohol per c.c. was then calculated (1) from the weighed quantities taken, on the assumption that no change of volume had taken place on mixing, (2) from the density of the fluid mixture. The following are the results:—

				Grm. mols. alcohol per c.c.	
				Actual.	Calculated.
Mixture 1	-	-	-	·0001998	·0002005
„ 2	-	-	-	5114	5138
„ 3	-	-	-	8626	8675

Rate of Expansion.—Thus far the conditions under which the colloid has been examined have been statical, that is to say, the colloid has been placed in the mixed liquids and left until equilibrium has been established. The simplest dynamical relationship is the rate of expansion of the colloid when placed in a single fluid. This is easily determined by placing a piece of weighed rubber in the liquid and transferring it at stated intervals into the paper-lined weighing-tube, in which it is then weighed after removing the paper (Method B). The total volume at the end of each period is easily calculated from the weight of the original rubber and that of the absorbed carbon bisulphide, on the assumption that the volumes are additive. This has already been proved to be the case. The expansion is at first very rapid, but soon decreases, and it was found to agree for a considerable distance with the equation $V = k \log t$, where V is the total volume at any moment, t the time elapsed, and k a constant. This is shown by the following results, the interval (about 3 minutes) required for each weighing not being included in the times stated.

Rate of Expansion with Carbon Bisulphide.

Vo. (cal. on 1 c.c. of rubber).	Time elapsed.	k .
1·0000	0 min.	—
2·3541	5 „	3·37
3·8198	15 „	3·25
4·9241	30 „	3·33
5·8771	60 „	3·31
6·2527	90 „	3·20
6·4079	120 „	3·08
6·5394	185 „	2·88
6·5615	245 „	2·75
6·5728 (max. vol. actual)	305 „	2·64

As the maximum volume is approached the value for k rapidly drops, either because the limit of elasticity of the rubber is reached or because the osmotic pressure of the diffusing liquid becomes balanced by the volume elasticity of the rubber. Since different maximum volumes are obtained with different substances (relative max. vol. with carbon bisulphide = 100, with chloroform = 112, with benzene = 91, and with ether = 54), the former conclusion cannot be correct, hence the latter conclusion must be accepted. If the rubber were unvulcanised it would dissolve completely in the carbon bisulphide; hence we must suppose that the coefficient of volume elasticity of unvulcanised rubber gradually becomes less as the volume increases, or that it is so small that it never balances the osmotic pressure, or only does so when the volume has become very great. The latter conclusion seems the more probable. The rapid drop in the value of k in the above results could be explained by the supposition that k represents a molecular friction or a sorting of the diffusing substance, since the friction would become *nil* when the osmotic

pressure became balanced by the elasticity of the colloid and the latter ceased to expand.

In another series of experiments, in which the weighings were made at shorter intervals, the following results were obtained, the time of weighing not being included in the times stated:—

Vol. (cal. on 1 c.c.).	Time elapsed.	K.
1.0000	0 min.	—
2.1355	5 "	3.06
3.0061	10 "	3.01
3.6988	15 "	3.14
4.2141	20 "	3.24
4.6569	25 "	3.33
5.0204	30 "	3.40
5.2990	35 "	3.43
5.7507	50 "	3.38
6.0510	65 "	3.34
6.2555	80 "	3.29
6.4797	110 "	3.17
6.5787	140 "	3.07
6.6674	200 "	2.90
6.6843	280 "	2.73

The values for k are probably not so accurate in this as in the previous series, since during the weighing the carbon bisulphide would tend to become equalised through the mass of the colloid, and the conditions would be proportionately disturbed. A linear measurement of the expanding colloid would give more accurate results, as it could be made without disturbing the conditions of the experiment.

The equation $V = k \log t$, representing the expansion of vulcanised caoutchouc when placed in carbon bisulphide, does not seem to be related to Fick's law for diffusion. That the conditions of the diffusion of carbon bisulphide into rubber are different to those of the diffusion of one liquid into another, is evident from the fact that the volume attained by the rubber is independent of the amount of carbon bisulphide taken, provided the latter is in excess. The diffusion of the carbon bisulphide continues until its pressure is balanced by the volume elasticity of the colloid, so that only one of the constituents diffuses. When ether is placed in contact with water, on the other hand, they each diffuse into one another. The regularity of the diffusion which allows it to be represented by the above equation is probably due to the fact that with pieces of tubing two parallel surfaces are presented to the liquid, the surfaces of the ends being negligible. There is therefore very little strain in the rubber. With pieces of rubber cord the same regularity was not observed. If similar conditions to the above hold for "soluble" colloids, then we can say that their slow diffusion is due to the opposition offered to the diffusion of the solvent into their substance by their volume elasticity instead of referring it to their large molecular weight. If the volume elasticity is small the colloid will dissolve in all proportions.

Relative Values of "k" for different Substances.—In order to find the relative values for " k " for different substances in the equation $V = k \log t$, the following method was devised in order to correct the variable value for the elasticity of the colloid. A piece of rubber tubing was weighed after $\frac{1}{2}$ hour in carbon bisulphide, and the value k_1 calculated. It was exposed to the air until the carbon bisulphide had completely evaporated, and was then placed for $\frac{1}{2}$ hour in the liquid under examination, weighed, and the value k_x calculated. Lastly, it was again dried, and placed once more in carbon bisulphide, and the value k_2 calculated. It is evident that the rate of expansion in the liquid x will be to the rate of expansion in carbon bisulphide as $\frac{k_x}{\frac{1}{2}(k_1 + k_2)}$. In this way the relative

velocities of diffusion of carbon bisulphide, ethyl iodide, chloroform, benzene, and ether were determined. The following are the results:—

		<i>k</i> .	
		For 30 min.	For 90 min.
Carbon bisulphide	-	1.000	1.000
Chloroform	-	.838	.976
Ethyl iodide	-	.668	.794
Benzene	-	.655	.754
Ether	-	.570	.553

Of these substances two are heavier than carbon bisulphide and two are lighter. Now the initial velocities of diffusion of the denser substances are *inversely* as their densities as compared with that of carbon bisulphide, whilst the velocities of the lighter substances are *directly* as their densities. Thus:—

	<i>k</i> (30 min.).	Density of CS ₂ .	Density of subst.
		Density of subst.	Density of CS ₂ .
Carbon bisulphide	1.000	1.000	1.000
Chloroform	.838	.848	
Ethyl iodide	.668	.669	
Benzene	.655	—	.686
Ether	.570	—	.568

So that if the densities of the substances be plotted as abscissæ and the values for *k* as ordinates, a curve will be obtained which will rise rapidly to a maximum for carbon bisulphide and then gradually decrease. This result is very remarkable. It is difficult to see what property reaches a maximum in carbon bisulphide.

A more understandable relation is got by comparing the mean velocities of diffusion with the molecular volumes. It will be found that they are inversely as the latter. Thus:—

	(mean).	Mol. vol. of subst.
		Mol. vol. of CS ₂ .
Carbon bisulphide	1.000	1.000
Chloroform	.907	.910
Ethyl iodide	.731	.784
Benzene	.704	.689
Ether	.561	.639
Turpentine	.361	.344

but the agreement is not so close here as in the relation involving the densities.

The two relations given above, one referring to the density of the substance and the other to the molecular volume, cannot both hold good for all substances, since by polymerising a substance the molecular volume may be increased indefinitely, whilst little change is produced in the density. As a matter of fact, the value for *k* for turpentine is in accord with its molecular volume, whilst it has only one-half the value it should have if the relation for densities held good, thus

$$\frac{\text{density of turpentine}}{\text{density of CS}_2} = .685.$$

At this rate isoprene C₅H₈ would conform to both relations.

This would seem to show that the relation involving the densities holds only for the simplest types. According to the second relation found, substances diffuse into rubber the more readily the smaller their molecular volumes, a result which one might expect. It is true that no note is here taken of the configuration of the molecule, which is generally considered to have an important influence on the solution of substances, but this factor may be involved in the *affinity* between the rubber and the substance.

This affinity is large in the case of the five substances considered, since they all expand rubber to a large extent, and it is obvious that the above laws can only hold good when the substance dissolves freely in the rubber. For instance, alcohol has about the same molecular volume as carbon bisulphide, but does not penetrate rubber at all; acetone, with a slightly larger volume, dissolves in rubber only with extreme slowness, producing a slight increase in volume. We may say, then, that when the force urging the molecules is large, they enter with a speed inversely as their molecular volumes, or, in other words, that the rubber seems to act as a sort of sieve. The above method of weighing a piece of rubber tubing after it has remained in a liquid for a given time, and calculating the velocity of diffusion, may prove a valuable means of determining molecular volumes, and hence of molecular weights, and could be applied to a number of inorganic liquids such as the chlorides of boron, silicon, tin, phosphorus, arsenic, and antimony.

The above relation for the diffusion of liquids into rubber involving the density is in accord with Graham's rates of "transpiration" of gases with the remarkable difference that the law is reversed; that is, when the gas is lighter than the reference substance (oxygen) its speed of transpiration is *inversely* as the densities, and *vice versa*. Thus:—

	Rate of Transpiration (Graham).	Density of subst. Density of Oxygen.	Density of Oxygen. Density of subst.
Oxygen - - -	1.0000	1.0000	1.0000
Air - - -	1.1074	—	1.1056
Nitrogen - -	1.141	—	1.143
Nitric oxide -	1.141	—	1.066
Carbonic oxide -	1.145	—	1.143
Nitrous oxide -	1.335	1.375	
Hydrochloric acid -	1.358	1.141	
Carbonic anhydride -	1.370	1.375	
Chlorine - - -	1.500	2.219	
Sulphurous anhydride	1.538	2.000	
Hydrogen sulphide -	1.614	1.062	
Methane - - -	1.815	—	2.000
Ammonia - - -	1.955	—	1.882
Ethylene - - -	1.980	—	1.143
Hydrogen - - -	2.288	—	16.
Carbon bisulphide			
(vapour) - - -	1.614	2.375	
Methyl Chloride	1.826	1.578	
Ethyl - - -	2.005	2.015	
Methyl oxide - -	2.072	1.437	
Ethyl - - -	2.273	2.922	

It will be seen that the relation holds good for the more permanent gases—oxygen, nitrogen, nitric oxide, carbonic oxide, nitrous oxide, carbonic anhydride, and ethyl chloride; whilst of the remaining gases, those near their liquefying points, viz., chlorine, sulphurous anhydride, ether, and carbon bisulphide, have rates of transpiration less than the calculated values. This would follow from the law which I have found for the transpiration of liquids (into rubber), for the first three substances when liquefied would probably have rates of transpiration much smaller than unity. So that we have here evidence of incipient liquefaction, just as we should have if we were to examine these substances in relation to Boyle's law.

The substances now left are hydrochloric acid, hydrogen sulphide, methane, ammonia, ethylene, methyl chloride and oxide. These all show rates of transpiration greater than the calculated values except methane. They are all compounds of hydrogen or methyl, and it will be noted that the rate of transpiration of hydrogen is greater than that of any of the

substances examined. This is in accordance with the fact that hydrogen is a gas "plus que parfait," that is, that its molecular volume (van der Waals' "*b*") is much greater than that of other gases. The same characteristic seems to apply to methyl.*

If we reverse the second law which I have found for liquids, it will stand "rates of transpiration are *directly* as the molecular volumes." On glancing over Graham's rates it will be seen that this is approximately the case, compounds of hydrogen and methyl excepted; that is, the rates of transpiration of gases increase with molecular complexity. If we knew more of the actual volumes of gaseous molecules (van der Waals' "*b*") we should be able to examine this relation more fully.

The consideration of the diffusion of liquids into rubber as a case of transpiration seems to be allowable, since gaseous transpiration is not confined to fine tubes, but was found by Bunsen to apply to ordinary gaseous diffusion when the diaphragm was thick, as when plugs of plaster of paris were used.

The standard substances, viz., oxygen in Graham's experiments on gases and carbon bisulphide in the above experiments with liquids, appear to be the substances which have the smallest molecular volumes in their respective states, viz., gas and liquid.

It is not easy to see why increase of molecular volume should increase the rate of transpiration of gases, except that the impacts would be more frequent, which would lead to an increased facility "in turning corners." That a highly tenuous gas has some difficulty in doing this seems to be proved by some recent experiments of Dewar, in which mercury vapour diffused from a small to a large bulb through a small aperture, both bulbs being vacuum, the presence of mercury vapour in the larger bulb being made evident by the application of a low temperature. The vapour passed with extreme slowness from one bulb to the other, although when the mercury was transferred to the large bulb a mirror was easily obtained by the application of liquid oxygen to the outside of the bulb. The interstices in rubber are probably much smaller than those in capillary tubes or plaster of paris, since transpiration phenomena cannot be obtained with gases through rubber. With such small interstices, smallness of molecular volume would be advantageous to diffusion. Moreover, the impacts of the molecules of liquids are so frequent that their ability to turn corners is practically infinite.

Referring once more to the transpiration of gases, we have the following values for density (mol. weight) and rates of transpiration:—

	Mol. weight.	Rate of transpiration (mol. vol.).
Nitrogen	28	1.141
Carbonic oxide	28	
Nitric "	30	
Oxygen	32	1.000
Nitrous oxide	44	1.335
Carbonic anhydride	44	
Ethyl chloride	64.5	2.005

It will be seen that with gradual increase of molecular weight the rate of transpiration falls to a minimum, and then again increases. If the molecular volumes (actual) are proportional to the rates of transpiration, then we have here something analogous to the relation of the atomic volumes of the elements to the atomic weights in each series of the periodic arrangement.

In comparing the transpiration of liquids and gases, it may be noted that the liquids enter the rubber in virtue of a "pull," whilst gases transpire through tubes in virtue of a "push." This difference may perhaps account for the inversion which has been described.

* Methyl compounds stand somewhat apart from their homologues in solubility and chemical properties. Thus methyl alcohol is insoluble in carbon bisulphide, its homologues are soluble.

The above relations between velocity of diffusion and molecular volume for liquids will furnish a means of determining the distribution of the two liquids (carbon bisulphide and benzene, for instance) inside and outside the rubber in the statical experiments already described. For if rubber when placed in a liquid expands according to the equation $V = k \log t$, then it is reasonable to suppose that if the distended rubber were placed in some other liquid, which was continually renewed, it would contract along the same path and with corresponding speeds, that is, rapidly at first and afterwards more and more slowly, so that k would remain the same. Now let a piece of rubber be placed in a mixture of carbon bisulphide and benzene until equilibrium is reached, and let there be a c.c. of carbon bisulphide and b c.c. of benzene per c.c. of fluid inside the rubber, and let there be a' c.c. and b' c.c. respectively outside the rubber, and let v_1 and v_2 be the molecular volumes of carbon bisulphide and benzene respectively. Then the velocity with which carbon bisulphide will diffuse in will be $\frac{a'}{v_1}$ and that at which it will diffuse out will be $\frac{a}{v_1}$, and since there is equilibrium $a' = a$. In the same way $b' = b$, that is, the density of the fluid will be the same inside and outside the rubber if the rates of diffusion are always inversely as the molecular volumes. This is the case with mixtures such as that of carbon bisulphide and benzene, in which both constituents enter the rubber freely "*per se*," but is not the case with mixtures such as that of carbon bisulphide and acetone. For acetone will penetrate rubber easily in the presence of carbon bisulphide, but will not do so by itself. These two cases are exemplified by the following results:—

Densities of fluid mixture inside and outside the colloid
Benzene and Carbon Bisulphide.

Vol.	Sp. gr. inside.	Sp. gr. outside.
100.00		1.2630 (carbon bisulphide alone).
102.62	1.2441	1.2461
103.24	1.2280	1.2345
104.54	1.2103	1.2149
105.31	1.2037	1.2079
105.65	1.1898	1.2000
106.13	1.1778	1.1874
105.82	1.1714	1.1817
106.40	1.1603	1.1687
106.82	1.1496	1.1598
107.07	1.1413	1.1511
107.29	1.1304	1.1390
99.51	.9198	.9233
98.22	.9068	.9103
96.70	.8957	.8978
95.29	.8847	.8864
91.41		.8671 (benzene alone).

Acetone and Carbon Bisulphide.

Vol.	Sp. gr. inside.	Sp. gr. outside.
100.00		1.2723 (carbon bisulphide alone).
102.58	1.2541	1.2508
103.76	1.2369	1.2350
104.14	1.2022	1.2045
100.57	1.1698	1.1632
86.93	1.1258	1.1020
71.52	1.0983	1.0564
58.76	1.0909	1.0203
32.77	1.0634	.9242

If we compare the quantities of carbon bisulphide per c.c. of fluid mixture inside and outside the colloid, we shall see that the carbon bisulphide is at first practically "level," but afterwards it preponderates inside the rubber as the volume decreases.

Grm.-mols. of Carbon Bisulphide per c.c. of fluid mixture inside and outside the colloid

Carbon Bisulphide and Acetone.

Vol.	Grm.-mols. of carbon bisulphide per c.c. inside.	Do. outside.	Ratio $\frac{\text{outside.}}{\text{inside.}}$
102.58	.01609	.01598	.993
103.76	.1548	.1541	.995
104.14	.1424	.1433	1.006
100.57	.1309	.1286	.982
86.93	.1168	.1085	.929
71.52	.1070	.923	.862
58.76	.1043	.795	.762
32.77	.945	.453	.479

Carbon Bisulphide and Acetic Ether.

Vol.	Grm.-mols. per c.c. inside.	Do. outside.	Ratio $\frac{\text{outside.}}{\text{inside.}}$
102.19	.01593	.01609	1.010
103.72	.1525	.1558	1.021
105.44	.1296	.1342	1.036
105.16	.1239	.1264	1.020
101.14	.1111	.1129	1.016

In both these cases the proportion of carbon bisulphide inside the rubber is least when the volume of the latter is greatest, either because the mass of rubber per unit of volume is least when the volume is greatest, and therefore the quantity of "attracted" carbon bisulphide is least, or because the acetone or acetic ether can penetrate the more easily the greater the distention of the rubber. We are now in a better position to understand the previous statistical results which should perhaps have been used to calculate the composition of the *fluid mixture* inside and outside the rubber. For let p be the number of gm.-molecules of acetone per c.c. of fluid mixture inside the colloid, p' the amount outside, and let a and a' have the same values as before. Then $p - ap^2$ will be the pressure of the acetone inside the rubber. This is balanced on the one hand by the volume elasticity of the rubber Kv , and on the other by the acetone outside, whose pressure is $p' - a'p'^2$. Hence.

$$p - ap^2 = p' - a'p'^2 = Kv,$$

or

$$\frac{p + p'}{2} - \frac{ap^2 + a'p'^2}{2} = Kv.$$

If A is the mean between a and a' , this expression becomes

$$\frac{p + p'}{2} - \frac{A(p^2 + p'^2)}{2} = Kv,$$

if a and a' do not differ greatly. And if p and p' are not widely different, the last equation will be equivalent to

$$\frac{p + p'}{2} - A \left(\frac{p + p'}{2} \right)^2 = Kv.$$

This equation is the one which has already been arrived at empirically, except that p in the previous equations represented the number of gm.-molecules of acetone per c.c. of expanded rubber instead of per c.c. of fluid mixture in the rubber. The above equation takes no note of

the initial unequal distribution of the acetone inside and outside the rubber, hence the equation should perhaps be

$$k(p - ap^2) = k'(p' - a'p'^2) = Kv.$$

A more rigid examination would be effected by taking into account the carbon bisulphide as well as the dissolved substance. The equation would then be

$$P - AP^2 + p - ap^2 = KV,$$

where V would equal the total change in volume which the original rubber undergoes, P and p being the mean number of grm.-mols. of carbon bisulphide and the dissolved substance respectively. The displacement of carbon bisulphide by the dissolved substance is not very great at first; hence the omission to consider it would not have much effect on the early part of the curve, but later it would be considerable. This may account for a part of the divergence of the calculated from the observed curve. I hope to work out this consideration at a later date.

Analogy between Vulcanised Caoutchouc and other Colloids.

Colloidal Sulphides.—The previous results seem to throw the most light on the so-called colloidal solutions, such as the sulphides of the heavy metals, ultramarine, &c. These may be considered to consist of particles of the insoluble colloid distended by the osmotic pressure of the water, there being an affinity between the colloid and the water just as there is between vulcanised caoutchouc and carbon bisulphide. The existence of such an affinity is likely since the colloidal sulphides are hydrated bodies. The particles are so small and so greatly distended by water that they remain in suspension, but they are sufficiently large and dense to partially reflect light. If now sufficient saline matter be dissolved in the water, its osmotic pressure will cause the colloidal particles to contract, just as acetone eventually causes rubber distended with carbon bisulphide to decrease in volume. The particles would then be much smaller and denser, and would sink and rapidly agglomerate together. If this explanation is correct a very small quantity of saline matter ought to distend the colloid particles to a greater extent than at first, and should reduce their opacity and rate of subsidence. Whether this is so or not I cannot say. I hope to make experiments on this point. In a similar way to the above the precipitation of soap by common salt may be explained.

Colloidal solutions, such as dialysed silica, alumina, &c., appear to be abnormal, since they cannot be produced by the action of water on the dry substance. There is no form of silica, for instance, which will swell up and go into solution when placed in water. These solutions are, therefore, unstable, since the volume elasticity of the colloids is not balanced by the osmotic pressure of the water and the colloid always separates sooner or later, the water being squeezed out. For this to happen the water must pass from particle to particle of the colloid. If we suppose that free ions can do this whilst water molecules can not, we can understand the effect of small quantities of salts in accelerating the separation of the silica.

If friable silica be placed in strong soda solution it gelatinises and eventually dissolves. Here there is a strong affinity between the silica and the Na ions, and the osmotic pressure of the latter expands the silica much in the same way as carbon bisulphide expands or dissolves caoutchouc. It is known that silica when it dissolves dissociates only to a very slight extent into ions, hence it is allowable to consider it to be infinitely distended when it dissolves in soda. In this case the chemical affinity is used up in doing work in expanding the colloid, and very little heat is produced.

Gelatin, Wool, and Cellulose.—The relation between vulcanised caoutchouc and substances soluble and insoluble in it which have been examined, will probably be found to hold for gelatin; water taking the part of carbon bisulphide, whilst alcohol, acetone, sugar, &c., and possibly

salts, will be substances having no affinity for gelatin, and which will produce at first an expansion of the swollen gelatin and afterwards a contraction. Precipitants such as tannic acid, chrome-alum, &c., probably combine with the colloid, producing a larger molecule and consequent increase in the volume elasticity, just as sulphur chloride and sulphur unite together molecules of caoutchouc in the process of vulcanising ("On the Vulcanisation of Indiarubber," C. O. Weber, *Journ. Soc. Chem. Ind.*, 1894, p. 11). It is well known that certain dyes, such as violet of methyl-aniline, pass rapidly into gelatin, wool and silk, when these are swollen with water; hence there must be an affinity between these substances and the dye, and it may be possible to determine the molecular weights of such dyes by the extension of a silk thread when placed in their solutions. Such a result would tend to confirm the view that dyeing is a case of solid solution, at any rate in its more elementary aspect. It is also possible by means of the above results to make clear an old phenomenon, which I believe has not yet been explained and which is as follows: If a piece of filter-paper be suspended with one end in a solution of a salt, such as ferric chloride, the salt will rise in the paper along with the water, but will stop short at a considerable distance from the highest point reached by the latter. Now since the water drawn up is continually evaporating, each succeeding portion of the cellulose will be swollen to a less extent. Further, if the composition of the fluid mixture inside the rubber be examined in the acetone experiments (pp. 182-183), it will be seen that the proportion of carbon bisulphide increases as the volume of the rubber decreases, so that the internal fluid would consist entirely of carbon bisulphide when the rubber had contracted sufficiently. If now we write water in the place of carbon bisulphide, and ferric chloride in that of acetone, it is evident that the iron salt will soon be squeezed out and left behind, assuming that there is no affinity between the iron salt and the cellulose, which is probably the case.

Metals.—The relations which have been found for the solubility of substances in caoutchouc will, I think, apply with considerable facility to the influence of dissolved substances on the physical properties of metals. There seems to me to be very good reasons for regarding the metals as colloids, amongst which are their malleability, ductility, and elasticity, the slow softening which some of them undergo when heated, the absence of any definitive molecular weight (Dulong and Petit's law refers to the atom); but most of all the nature of metallic solutions. If a piece of tinned copper be placed in molten tin at a definite temperature, some of the copper dissolves in the tin and the latter probably dissolves to a certain extent in the solid copper. If the temperature be raised, greater quantities dissolve and finally the two metals mix completely, forming a homogeneous liquid. If now the mixture be cooled, the copper does not crystallise out but the two substances generally set as a whole. This behaviour distinguishes the alloy from all solutions of crystalline substances, but not from solutions of colloids such as gelatin. For if the latter be placed in water it swells to a certain extent. If the temperature be raised more water passes into the colloid, and finally when the colloid is "melted" it mixes in all proportions with the water. Now if the solution be cooled, no separation of the gelatin and water takes place but the mass sets as a whole; so that we have here a complete analogy if we consider the copper as being sometimes a colloid. It may be noted that the most malleable metals are those which crystallise in cubes. With three equal axes, the confused arrangement representing a colloid would probably be most easily produced. Now if we return to the rubber expanded with carbon bisulphide, it may be assumed that its tenacity will be less the greater the extension. Now let the carbon bisulphide be gradually replaced by other substances. The effect at first will be the same for all, the substance will exist in the rubber in a "gaseous" state, and the expansion

* The term 'gaseous' has been used here and in other places for want of a better one, to indicate that state of matter in which the molecules exert no influence on one another.

will be proportional only to the number of molecules per unit volume; but if further quantities be added the result is very different. If the substance has no affinity for rubber as in the case of acetone, the negative pressure " ap^2 " will rapidly neutralise its osmotic pressure and the rubber will soon contract, the maximum volume in the case of acetone being only 104. If, on the other hand, the substance has an affinity for rubber, as in the case of benzene, the negative pressure will be $(a - A)p^2$, that is, it will be small, the substance will remain "gaseous" a much longer time and a proportionately larger volume will be reached, viz., about 107, although benzene "*per se*" can only produce a volume of 91. Now those substances which are most injurious to iron, viz., sulphur and phosphorus, are those which can mix with it in all proportions, and which therefore have a large affinity for iron and would be able to produce a large distension. Moreover, we see that the effect of any one element will be influenced by those already there. Thus, if we gradually replace carbon bisulphide by benzene, the maximum volume attained is greater than that produced by either substance alone; in the same way it is known that the effect of aluminium, silicon, and other elements in modifying the properties of iron depends on the presence of carbon. We may suppose, then, that when these elements are added to iron charged with carbon they at first all produce a slight expansion, which is unimportant, until the maximum volume is reached, and then the volume of the iron begins to decrease and its tenacity and elastic strength to increase. On the other hand, sulphur and phosphorus as already explained produce a considerable expansion before the maximum volume is reached. The distended metal is then near its elastic limit and is consequently very sensitive to shock.

Of course, when we are adding one element we shall be taking away another, but not in equal amount so far as the total mass of iron is concerned. Thus, referring to the original carbon bisulphide and acetone experiments, and considering the constituents inside the rubber only, we have the following results:—

Vol.	Inside.		Vol. of added constituents (expansion).
	Grm.-mols. CS ₂ per c.c.	Grm.-mols. acetone per c.c.	
100.00	0.01424	0.	86.70
102.58	1376	0.00046	89.28
103.76	1330	89	90.46
104.14	1229	178	90.84
100.57	1122	259	87.27
86.93	977	344	73.63
71.52	861	396	58.22
58.76	799	394	45.46
32.77	538	339	19.47
13.3	0.	0.	0.

So that for each state of equilibrium as the volume is decreased we must gradually displace the carbon bisulphide by acetone. Now it is well known that the effect of aluminium and silicon is to displace carbon, which separates in the form of graphite, and such graphite must be considered to be external to the system. To produce a volume of 107 would be impossible with a mixture of carbon bisulphide and acetone, but it could be effected with one of carbon bisulphide and benzene. For benzene we must read phosphorus or phosphide of iron in our "iron" analogy.

In the rubber experiments the constituents inside the colloid are balanced by those outside. This is probably also the case when the metal is submerged in the impurity-giving slag. On cooling some of the constituents may crystallise out. These would be considered to be external to the metal. That such a balance between fluid mixture inside and fluid mixture outside the metal really exists, at any rate when the metal is red hot, is proved by the experiment of M. Lencauchez (Roberts-Austen's "Introduction to Metallurgy," p. 74), in which iron was maintained

at a red heat for 100 hours in order to allow fluid constituents to diffuse out. At the end of the experiment the metal was found to be coated with grains of slag which had sweated out, the following being the composition inside and outside the metal :—

	Iron.	Slag.
Phosphorus - - -	1.9 per cent.	4-6 per cent.
Silicon - - -	2.6 "	0.6-0.8 "
Graphite - - -	} 3.5 "	0-1.5 "
Combined Carbon -		0-1.24 "

If the exuding fluid were continually scraped off a simple method of removing phosphorus would be the result, but it would be a very slow one.

Another fact bearing on the idea of a constituent, so dilute as to be "gaseous," acting in opposition to the volume elasticity of iron, is the statement of Roberts-Austen that the tensile strength of electrolytic iron containing 250 times its volume of hydrogen is only 2.7 tons per square inch, whilst after annealing it rises to 15.5.

There are necessarily many considerations which will modify the final result, but it seems to me that it is only by some such theory as the above that it is possible to account for the extraordinary effect which is in some cases produced by small quantities of substances dissolved in iron.

I ought to have pointed out that the boiling-points of phosphorus and sulphur being low as compared with those of other elements found in iron, " α " will be small and ($\alpha - A$) will be still less. These elements should therefore be highly "gaseous" when dissolved in iron.

Another property of metals of wider application is the change in tenacity produced by the addition of very small quantities of other elements, and which depends only upon the atomic volume of the added element. The following are the atomic volumes of iron and the elements with which it is usually alloyed :—

Carbon - - -	3.6	Chromium - - -	7.7
Boron - - -	4.1	Tungsten - - -	9.6
Nickel - - -	6.7	Silicon - - -	11.2
Manganese - - -	6.9	Arsenic - - -	13.2
Copper - - -	7.1	Phosphorus - - -	13.5
Iron - - -	7.2	Sulphur - - -	15.7

If the added element has an atomic volume greater than that of iron, the tenacity of the latter is increased, and it assumes the hard dense " α " modification. On the other hand, if the dissolved element has an atomic volume less than that of iron, the tenacity is decreased and the iron is found to be in the soft less dense " β " condition. This change of tenacity is not confined to iron but has been shown by Roberts-Austen to apply equally well to gold and other metals, and it is brought about by very small proportions, so that it cannot depend upon the mutual attractions of the "foreign" atoms for one another, but is determined solely by the volume of the atoms relative to those of the metal in question.

I think the effect can be based upon the volume elasticity of the metal, bearing in mind the fact which was pointed out by Prof. Fitzgerald in the last Helmholtz lecture, that although in dilute solutions the dissolved molecules have an osmotic pressure comparable with those of gasses, yet they do not share the easy compressibility of the latter, and can only suffer change of volume under very great pressure.

For this purpose, suppose that a single atom of iron in a mass of the metal be replaced by one of copper. The new atom will exactly fill the space occupied by the displaced one, and will exert an equal pressure. Hence there will be no change in the equilibrium of the parts of the metal, and the mutual attraction of the iron atoms will be balanced by their impacts one on the other exactly as before. If, on the other hand, an atom of iron be replaced by one having a greater atomic volume, the atoms of the iron will be thrust asunder to make room for it since the dissolved atom is practically incompressible. Hence the atoms of the metal inside

the mass, including the new atom, will be subjected to a pressure by the volume elasticity of the metal. The latter will then be in the compressed or dense " α " modification. Lastly, if the added atom have a less volume than the displaced iron atom, it will exert a less pressure than did the iron atom, the surrounding atoms will close in on it, and the iron will be strained in virtue of its volume elasticity in the opposite direction, so that the metal will be in a stretched condition and will form the less dense " β " modification.

Since colloids may be looked upon as liquids which have failed to crystallise, and may be considered to have many of the properties of liquids, the above considerations may perhaps be applied generally to liquids and concentrated solutions. If this is done, we are able to explain the slight expansions and contractions which take place when organic liquids are mixed. Such changes of volume would not produce any very marked change in properties in the case of liquids, but might very well account for the differences between α and β iron, as already explained. Expansions never take place in making dilute solutions of electrolytes, but always contractions. The strain to which the liquid molecules are submitted might perhaps account for electrolytic dissociation.

Another property of metals which may be explained by the application of van der Waals' equation to dissolved substances is liquation. When a mixture of metals is cooled, a partial separation takes place after solidification, and the constituent of lowest melting-point is always found to have travelled inwards towards the centre. The same is found to be the case with the non-metallic impurities in iron. Now I have considered the outward pressure of a dissolved substance to be $p - ap^2$, or more fully $p - (a - A)p^2$, where ap^2 is the inward pressure due to the attraction of the atoms of the dissolved substance for one another, and Ap^2 the outward pressure due to the attraction between the substance and its solvent—"a" being always greater than "A." Now, as the temperature falls the outward "gas"-pressure " p " decreases and the whole expression becomes negative, the result being that the still fluid constituents will be drawn inwards. As the force "A" is due to the mass of the solvent, its effect will be to direct the condensing substance towards the centre of gravity of the mass.

If the metal be cooled with extreme slowness, liquation takes place to a much less extent, which may perhaps be explained by supposing that the solvent mass crystallises. Diffusion through its mass might then be impossible, since there is no tendency for crystalline solids to diffuse into one another, nor for a liquid to diffuse through a crystalline solid. Solids, on the other hand, will diffuse into colloids. Thus, Sir Frederick Abel has shown that a highly-carburised iron plate will lose carbon to a non-carburetted one even at the ordinary temperature if they are tightly pressed to gether. Again, solid sulphur will diffuse easily into caoutchouc. The above explanation of liquation would perhaps apply to the separation of flints in chalk, especially as the alkalis in the soil would render the siliceous *débris* somewhat soluble. As the molecular weight (or volume) of gelatinous silica is very great, the separation would be very slow.

In connection with the diffusion of colloids into colloids, it would be interesting to see if colloidal sulphur will vulcanise caoutchouc more rapidly than the crystalline element.

Analogy between the Action of Dissolved Substances on Swollen Colloids and on Freezing Liquids

It is usually considered that a liquid in the act of freezing is not homogeneous. In some parts of it the molecules are brought together sufficiently closely that they are in the act of forming crystals; in other parts this is not the case. If the molecules forming the "nascent" crystals be considered to represent the colloid in the above experiments, and the other portion of the freezing liquid to represent the fluid surrounding and penetrating the colloid, the first effect of the addition of dissolved

substances to the freezing liquid will be to drive asunder the crystal-formed molecules, just as dissolved substances at first expand rubber; and from the above experiments the amount of separation will at first be equal for equal numbers of molecules of dissolved salt. The temperature must then be lowered, in order that the crystals may again begin to form; and since the separation of the crystal molecules is equal for equal numbers of molecules of dissolved salt, the lowering of temperature required will also be equal. This analogy between a colloid and the confused agglomeration of molecules representing a "nascent" crystal is rendered more reasonable if we consider a colloid to be intermediate between a liquid and a crystalline solid. The crystallisation of a colloid may either never take place or it may be postponed. The latter condition may apply to metals, and the imperfect separation of copper on cooling a solution of the metal in tin may be due to a tendency of the metal to crystallise: if it were a true colloid, the metallic mixture should always solidify as a whole. The crystallisation of steel under continued concussion would point to the same conclusion, viz., that the crystallisation has been postponed. Colloids, as we have seen, allow substances both solid and liquid to diffuse through their mass, and thus resemble liquids. Crystalline solids, on the other hand, do not allow of any diffusion through their mass. This is probably due to the short range of the forces which bind together the molecules of a crystal. If, for instance, ice be brought into contact with salt, there is probably an affinity between the two substances, just as there is between caoutchouc and carbon bisulphide; but in one case the molecules are torn asunder and separated from one another, the result being that there is a change of state and consequent great absorption of heat: in the other case the solid is simply submitted to a strain, and little or no heat is produced. That this is the case was proved by placing a piece of rubber tubing lightly over the bulb of a thermometer and immersing it in carbon bisulphide. No change of temperature took place. The fact that the heat of "solution" of colloids is practically nought is in favour of the view which has been put forward, viz., that colloids do not readily dissolve, i.e., separate into chemical molecules, but that the volume elasticity of the solid is simply infinitely strained.

Effect of Heat on Colloids.—Indiarubber is peculiar in its relation to heat, in that if it be stretched along one dimension and then be heated it contracts along that dimension and probably expands along the other two, so that the volume expansion is still a positive quantity. This, I think, can be explained on the assumption that there is some diffusing substance in the rubber whose osmotic pressure in all directions would be increased by the action of heat. Now, in the stretched rubber the material is expanded along the longer axis and is compressed along the shorter axes. If the osmotic pressure be now increased in every part, it will assist the volume elasticity of the rubber in those parts which are compressed, but will oppose it in those parts which are expanded; hence the displacement will be greater in the first case than in the second, and the rubber will expand along its shorter axes and will contract along the longer one. This action might be imitated by placing rubber in carbon bisulphide until it has completely expanded, stretching it, and then adding a small quantity of acetone or other substance to the fluid surrounding the rubber: a contraction ought to take place along the longer axis. I hope to carry out this experiment. The result, should it be of the nature expected, should have some bearing on muscle-action, since it would refer muscular contraction to a suddenly produced osmotic pressure.

The diffusing substance in rubber, to which it owes its contraction by heat when stretched, is probably some portion of it more fluid than the rest. The existence of such would be in accordance with the view that it is intermediate between a liquid and a solid, and as a matter of fact it is known that unvulcanised rubber contains two substances of different solubility in carbon bisulphide. The softening of rubber by heat also bears out its intermediate character. Again Mallock has shown that when rubber is greatly stretched it behaves like putty or wet sand, or any other

mixture of a solid and a liquid ("Physical Properties of Vulcanised Indiarubber," A. Mallock, *Proc. Roy. Soc.*, 1889, p. 233). Such a mixture stretches easily at first, but the expansion abruptly terminates when the fluid portion has been drawn into the interior. Mallock has shown that the same abrupt termination to stretching takes place with rubber.

It may be pointed out in passing that the unequal expansion by heat of crystals may be imitated by means of stretched rubber, the inequality probably depending in each case upon the nature and extent of the strain along the three axes. The previous results on the rate of diffusion of organic liquids into rubber show that this rate is inversely as the molecular volume, which would support the view that rubber has a sieve- or network-structure. Such a structure is also considered to represent the arrangement of the molecules in a crystal. It would be difficult to say what is the exact analogy between the two kinds of substances. If we divide correlated matter into liquids, colloids, and crystalline solids, we can say that in the first a strain is impossible, in the second it can be produced by external forces, whilst it exists in the third in virtue of the polar forces.

In the above work there are many points which require further investigation, but I am obliged to postpone this task, as even in its present state the research has involved a very large amount of work, including some 1,200 weighings and much tedious calculation.

